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117th Annual Convention

to be held at the
Grand Geneva
Resort & Spa

Lake Geneva, WI
June 20-23, 2023

For more information go to:
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116TH ANNUAL CONVENTION — JUNE 21–24, 2022

Opening Address

by **Michael Bley**

Finally, we are able to have our convention in person!

I want to welcome everyone to the 116th Annual Convention. Joe Hoefler was able to assemble a wide range of papers, you will hear during the next two days. I hope you enjoy the program as much as I expect everyone will. Take advantage of the social interactions & activities scheduled for the next few days.

Now, let me introduce Eric Webb from Stahl, the sponsor of the John Arthur Wilson Memorial Lecture.

Introduction to the 61st John Arthur Wilson Lecture

by **Eric Webb**

Good morning Ladies and Gentlemen! My name is Eric Webb and it is my honor to introduce this year's John Arthur Wilson Lecture. After the two year pause due to Covid it is a pleasure to be back to this year's conference. We all have been through some very difficult times and being able to attend the ALCA conference and see all your smiling faces is a welcome relief to these troubling two years we have endured. This is the 61st John Arthur Wilson lecture. Looking back at the former recipients of this award you will see strong leaders of our industry in various ways and this year's recipient is another strong leader.

The John Arthur Wilson lecture was initiated in 1959 in memory of the late John Arthur Wilson, who was regarded as a world leader in the leather chemical industry as well as an esteemed member of our association.

I am here as a representative of Stahl, who are proud sponsors of the John Arthur Wilson lecture since 2004. I know our association thanks Stahl for their ongoing support and commitment as the main sponsor for this lecture.

This year's recipient of the John Arthur Wilson award is a visionary who embraces lean and innovative manufacturing techniques while ensuring product sustainability. His passion and commitment to leather is evident in his leadership. He is the current CEO of Pangea, a global leader of artisan leather for the automotive leather industry. In his 25 plus year career in automotive he has held two key Leadership roles within the leather industry. Besides his current role of CEO at Pangea he held the role of Vice President of Operations at Eagle Ottawa, where he led the global standardization of the company's operation, material management, global engineering and human resources and it's ten manufacturing facilities worldwide.

He earned a Bachelor of Science in Mechanical Engineering from South Dakota School of Mines and an International Business MBA from Wayne State University. He currently serves as an advisor to Endeavor Detroit, which promotes mentoring to high-impact entrepreneurs in Michigan and is a member of the Private Directors Association of Detroit.

Ladies and gentlemen, please welcome this year's winner of the John Arthur Wilson lecture recipient Randy Johnson.

The 61st John Arthur Wilson Memorial Lecture

The Road Ahead

Randy Johnson

President & CEO

Pangea

The chemical profession has made innumerable contributions to the leather industry and the ALCA represents the best technology we have to offer. As creators and suppliers of leather, in honor of John Arthur Wilson, we take a moment to look back at all we have achieved. Despite the most recent couple of years of pandemic and the disruptions to our collective industries, there is much to celebrate. Let me first reflect on the history of leather.

Leather has been a noble profession for a thousand years, dating back as far as Stone Age, 400,000 years ago.

- Starting with the Bronze Age (pre-3000BC) leather making became more specialized and purposeful as veg tanning came to Greece in 200BC.
- Rome (600BC) used leather heavily in the military and in the Middle Ages (1300AD), bringing the first mechanical equipment to help produce.
- In the Renaissance Period of 1500AD we saw dramatic increases in specialty upholstery as the first tanning associations were started.
- In the Enlightened Age of 1700AD, control of production and raw material supply were prevalent. In North America the English forced the American Colonies to use British hides only restricting local trade.
- The Industrial Revolution (1800s), leather mechanization like splitting and drying were used to reduce the amount of labor.
- In the Victorian Age (1875+) Chrome Tanning was invented. This replaced veg tanning as it was faster, thinner and softer. The first synthetic leather (Presstoff) made from paper pulp was commercialized.
- The Progressive Era 1900-1950 saw the invention of plastics and rubber impacting leather demand. The term “Patent Leather” was used that described the new glossy finished leather.
- In the Modern Era (1950+) plus we saw a shift of production to lower cost regions as well as “Leatherette” made from PVC.

The tanner is a unique profession, one where the need to understand both physical properties and chemical reactions baffles lay persons to this day. The uniqueness of every single hide and the goal to produce a standard article from each unique raw material, is the alchemy output.

As we continue our efforts in uncertain times, we must also, as technicians, not forget that our work ultimately brings innovation and value. We must be the promoters of leather through these innovations. We need these innovations to become the history of our industry to compete with other materials, especially when many surface materials are commonly self-proclaimed as “leather-like”.

John Arthur’s book, *Modern Practice in Leather Manufacture*, is over 700 pages of facts and practices that we still use today. It is in many ways the Bible of leather manufacturing. This book documents not just tanning of leather, but definitions that we use commonly like Heavy Natives, Light Natives and Colorado’s. It also talks about Government controls and purchasing of “foreign” materials, to Chrome and Veg tan while it touches on new technical tanning concepts like Aldehyde, Tungsten, Syntans. This area of alternative tanning is where we need an updated version of the “Modern Practice”. Today, foreign material would be considered somewhat comical as our world and Wilson’s world are vastly different due to globalization and the “shrinking” of the world through social media, real time communications, and the difficulty of understanding what is accurate and what is “fake” or “bot-created”.

I am happy to write about a subject I have been involved in for nearly 20 years of my career – Leather Manufacturing. I am NOT a technical tanner. I am however in the small group of professionals that know how to make the material, stemming first from a great tannage and finish technology, and converting those routines into a high quality, repeatable product that our customers demand. I’ll present interesting facts about disruptions in the leather market for automotive and share some company marketing information we have developed for Electric Vehicle trends. I will also touch on sustainability, as we cannot ignore the perceptions and reality of our industry. I want to talk to you about how Sustainability and Lean Manufacturing are really connected to a core philosophy of waste elimination. And finally, I will give you some parting thoughts on your work in supporting ALCA and opportunities to Promote your magnificent work.

If we turn to the very first chapter, the first page of John Arthur’s work, we will see the major topic the industry has been challenged in the media amidst the opposing voices that speak so loud, we get drowned out.

The message sent by the leather industry back then is the same as it is now.

Meat determines the production of leather, presuming that meat demand exceeds leather demand. If that last presumption is not true, then hides go to a landfill. This scenario has happened over the last 5 years or so, an unprecedented recent reality.

Part of my message is for us to help our industry bring that awareness to the forefront of our customers' minds.

Pause, Portray and **Promote the Truth** about leather is the ultimate message. The work we do in this industry, and this association, forms the foundational content of our ability to compete. Converting a waste product into a luxury product is the poster child for Sustainability and Environmental Stewardship.

As we weave in the word “Sustainable” into leather nomenclature, leather is already the ultimate example of sustainability. Promoting Sustainable products and processes has now become the imperative optic of our industry.

Pangea and other auto leather companies have studied the consumer perception of leather. We've asked our customers, leather consumers, and we've crossed referenced research that has been done globally. These further statements are not anecdotal. This is statistically valid information of thousands of people in Europe and Asia and the United States. There are some interesting takeaways, showing consumers believe our product is premium and desirable.

The first thing we notice about consumer statements is: Leather is still seen as a luxury material, and they expect it in certain applications. When a customer buys a car with a surface material that is leather-like, they think it is authentic leather. Very, very few of them ask for Animal-Free surface material that feels like leather.

In fact, if they are in the premium car market or shopping for high-end sofas and chairs, consumers see it as a necessity. It is like a stamp of authenticity. Leather meets all expectations.

Back to the properties that Tanners create with this material, consumers want natural material for comfort, durability and cleanability. What does this mean?

Comfort and Durability: Pride of ownership results from this material and its natural feel and strong resistance to degradation.

Cleanability: And of course, in the modern world we're obsessed with cleanability due to things such as the pandemic.

These are the facts about consumers' desire for the real thing.

Finally, the studies show that consumers will pay for this material. In many markets from auto to furniture, people are paying for leather, only to find out they have PVC or PU. I can give you a dozen examples of dealerships vehemently saying PVC is leather.

At Pangea, we performed an internal and exhaustive study of the Electric Vehicle (EV) market amidst the concerns that EV means plastic-synthetic surface materials, led by the Tesla drive for animal free interiors.

Electric Vehicles in modern times, are a “re-start” of those developed in late 1800s. Production units were made in the teens and through the early 1930s where at one time EV's garnered 30% of personal vehicles. They declined rapidly with the introduction of the Ford Model T in 1910 and the discovery of cheap crude oil in Texas.

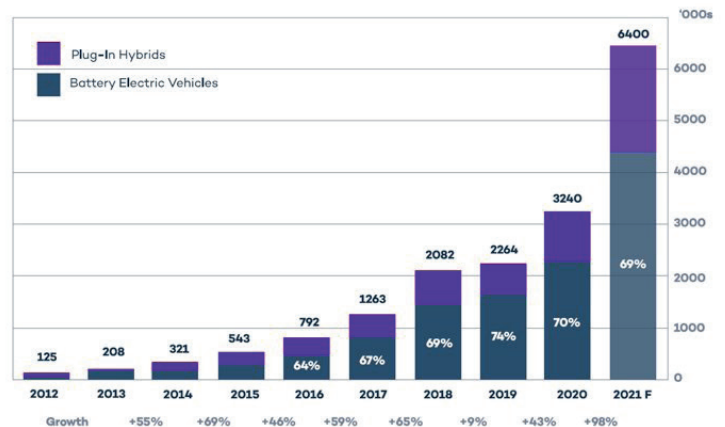
Therefore, EV's lost in the market due to higher cost and poor infrastructure.

With the recent rise of electric vehicles, and consumer awareness on sustainability, at Pangea we wanted to know: Does EV mean PVC surface material? We talked directly to consumers and our Original Equipment Manufacturer (OEM) customers to understand a little bit more about what the EV market looks like. We looked at this from a consumer profile point of view and how it may shape perspectives on leather. We have all seen the announcements:

- Honda pours \$40B into Electrification,
- GM plans to tie executive compensation to volume,
- Ford claims to go all in.

The sheer amount of capital investment into this segment will be the final deciding factor on how this chart of volume will look over the next 5 years, as well as Government incentives for infrastructure and consumers to buy.

Global plug-in vehicle sales



From our studies, what do consumers say about EV's and leather?

Consumer interest in EV's is shifting every day, in an increasingly supportive direction. But how does it look across the generations? The first overall observation is that the interest is strong across all age groups.

- 78% of Millennials (roughly 27-45 years-old) are interested in buying an EV.
- Current purchase statistics show that of the people who have purchased an electric vehicle, are millennial and Gen X's (roughly 46-57 years-old).

Now surprisingly, as it notes here, baby boomers have bought into the broader mix of green vehicles, Electric, Hybrid, Plug-in Hybrid, and Fuel Cell vehicles, whereas the stats above from Truecar are for electric specifically.

We can presume that Baby Boomers like the idea of a back-up to an All-Electric-Vehicle and hence the desire for Hybrid. The downside to Hybrids: two powertrain platforms.

The topics within these market trends are tightly tied to one another. Sustainability is all over the news, as well as is veganism. There's a growing awareness, trend, and desire for sustainability in all products.

Next, there are many who believe that vegans are a high-profile market driver of electric vehicles. Veganism as a movement has been around for many, many years and for this market segment and industry there are two things that stand out.

First, activists, no matter what they stand for, are very, very vocal.

But second, when you peel back and do the research, you find that statistically there's not more than a few percent of people per

population that are vegans. And of those, many do not stay vegan, and fall off the bandwagon over one to two years.

We need to pay attention to how Veganism is used. It is a mistake to put vegan and animal activism into the same bucket. One does not require the other. In conclusion, vegans simply prefer not to eat meat and their numbers really do not impact the buying volume for leather.

There certainly are a few OEMs that are Animal free in philosophy, and Polestar was one of them.

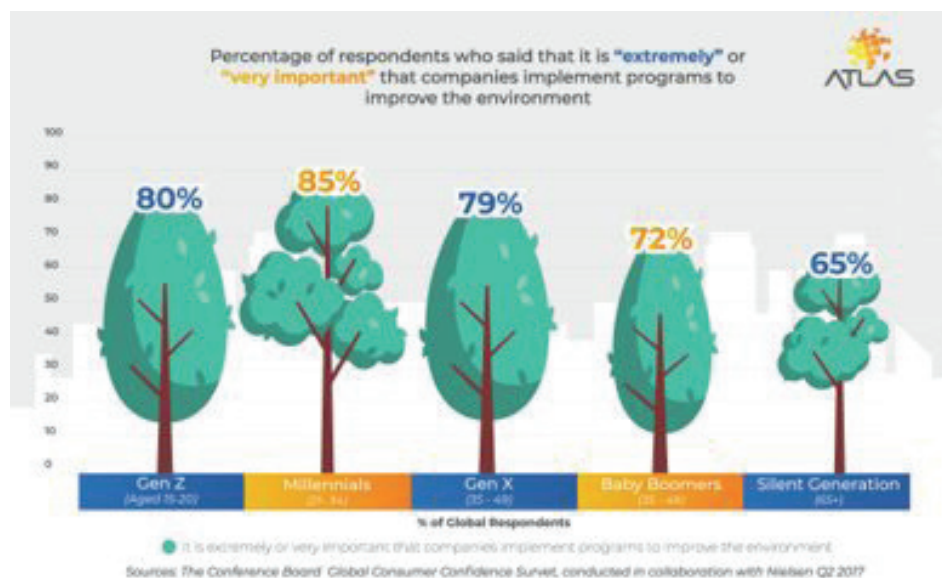
Polestar made a big deal about animal free interiors, but recently did a public turnaround in La Conceria "*The vegan car that quietly returns to leather*". Polestar is now offering Napa leather with sustainability credentials.

In Sweden, Polestar officials said that relying on synthetic materials has challenges in terms of sustainability, while on the other hand, leather is a solution for quality and environmental issues.

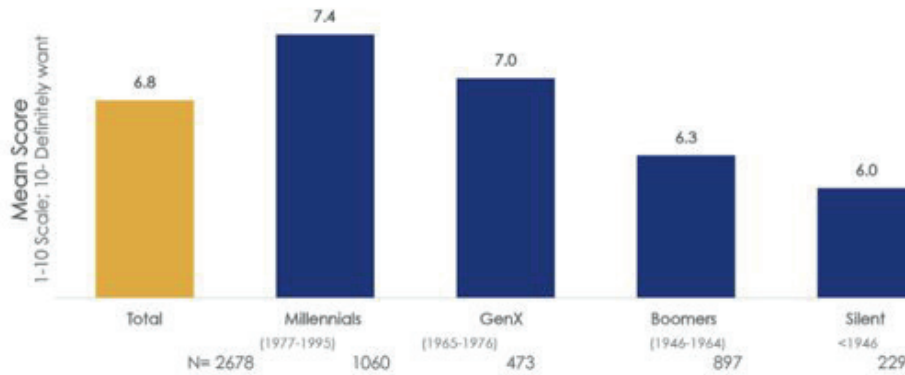
Industry executives frequently impress subjective opinions on the products they manufacture. Here I think, the market asked them to reconsider. Polestar listened – and shows a good sign for our industry.

The quotes here are the points we, as an industry, have been driving for. Polestar may lead the breakthrough and cause other nameplates to follow suit.

As in the previous discussion on generations and EV interest, we follow this same in this chart, where EVERY generation believes companies should focus on more environmentally friendly products.



Importance of leather versus generations



This chart is looking at consumers and their willingness to choose sustainable alternatives – and pay for them - slicing the data by generation. Taken together, this research can give us some idea of what’s going on with the general population. Over all generations, almost 60% of all consumers said they’re willing to change and consider and think about their purchasing habits just to help reduce waste and environmental impact. I know of no one in the world who doesn’t want clean water, vast open ranges, healthy air, less waste in the dump.

Leather and Generations: Let us look now at two different pieces of research. We looked at the same population group and asked 2 questions, the one on the left side is about sustainability and the willingness to pay up for it. And interestingly, the chart on the right is also by generation, it is the importance of leather to consumers and the willingness to pay for it.

The social chatter today about leather would suggest there is a negative correlation between the desire for EVs (Electric Vehicle) and Leather. Our research shows that leather is desired by all generations, as is an interest in more sustainable products.

So, our conclusion is that Electric Vehicles and the desire for leather are not in conflict. All generations want more sustainable products and all generations like and want leather.

Next, Autonomous Vehicles will benefit the leather market due to their cleanable and comfortable and durable physical properties.

Wards Automotive had a symposium and panel discussion about autonomous vehicles, their future on interiors, growth, and the role those different manufacturers can play.

One of the things that they found is when they talked to people about their thoughts about autonomous vehicles the most important things for the interior was that the surface was its cleanability and softness. Leather satisfies these requirements; cleanability, overall comfort and a match in softness.

Regardless of the electronic content in the car, there being no driver, and being able to wirelessly connect your phone - at the end of the day, you are going to be sitting in a vehicle. Consumers want that experience to be like a luxury sofa or chair. They want a clean and comfortable experience.

In current times, Ride Sharing means the use of a smart phone to connect with a driver and his vehicle. It also may mean sharing that ride with another passenger. This concept is quite different than that of the TAXI days, but the experience during the ride can be very similar.

When you take a cab, you know it’s a public space. It is typically a little unpolished frequently dirty, and mostly uncomfortable. And so, you try not to think about it. You sit there with your hands on your lap, and you just get where you’re going, and get out.

But when you’re requesting ride sharing, you’re sharing a personal vehicle. You may think about the look and feel more, AND pay more for a nicer ride (Uber Black, or Lift LUX)

Truthfully, ride sharing is another market for automotive leather.

The overall drive for non-leather surface material manufacturers is they want to promote a false idea that their material is leather. This is a core issue for our industry. In a free competitive market where most of the world supports, government regulation is intended to be used to create free competition. Synthetics are using unfair practices to achieve their business objectives.

When we look at companies that produce leather imitations, they shamelessly steal the noble name of leather and find a way to include it in the brand. When was the last time you heard one of these alternatives say, “Our is the best Poly Vinyl Chloride Material made from petroleum jelly in the market – buy ours”? They simply are embarrassed to tell you what their product truly is. Later I’ll speak to regulatory efforts.

Outrageous as it sounds, consumers are so confused on this concept of vegan leather that:

- 30% of them believe vegan leather is from the hide of an animal.
- And over half believe PU leather is also from the hide of an animal.

How? They have been purposely misled, and our industry has been slow to respond. So leather, truth, honesty, and materials suffer.

Our industry, due to its 400,000-year existence, contains a lot of negative baggage, and the pundits have taken advantage of this and are driving a negative leather narrative.

The reality is that many consumers have a perception of what leather is and it is our responsibility to change this largely untrue and negative narrative. Likewise, it is our responsibility to drive more awareness into the plastic-based alternative material.

In economics, there is a term called *externalities*. Think of externalities as negative byproducts. But these economic byproducts are generated when you are producing a good.

There are effects of production that are not captured into the price a consumer pays for the product. Consider a factory that uses water and electricity and does not clean its own water after use. Because of current regulations, that externality is not being paid for, except by the environment or local utilities.

These are External Costs that regulations and Sustainability are now addressing.

Moving beyond Externalities and Sustainability movements now, relative to hides – the best use of a hide is to find an additional product one can make versus landfilling. We have seen over the last couple of years, for the first time, that low grade hides have been dumped into landfill because the value of the end hide has a higher cost than to simply land fill. Landfilling costs of hides are not paid for if leather is not made, and from an environmental perspective has become an externality. Back to Wilson's comment... "The demand for meat drives the production of leather" - and my premise to add is - so long as demand stays strong with leather.

If indeed hides go into landfills the billions of pounds of waste could be staggering. And even with our best efforts today, not every hide gets made into leather. However, every hide that we do save from the landfill provides economic value.

Hides and leather are not the only byproducts or waste streams from converting cattle for beef.

Many parts of the animal that have nothing to do with the actual beef production are useful to society, and they provide value because they have a profit proposition. If leather demand drops precipitously, then hides will flood into other uses until those markets are saturated with supply. Ultimately non-leather use for hides is a finite market. People want the products that are made from parts of the animal (Such as vaccines, medicines, cosmetics, etc.) that are not converted into beef.

So long as the demand for meat continues to grow, supply of hides will fill a market *or fill the earth*. As leather professionals, we need to work to make sure that the inherent demand for leather is fulfilled, and not filled by materials that claim to be leather. To be clear, our studies confirm that there is plenty of demand for leather, sadly some of that demand is filled by deceptive material marketing practices.

Moving on to technical terms and branded terms, look at the words we use in our industry. To the lay person, these terms are mostly not understandable.

- | | |
|------------------|-----------------|
| • Alkalibacteria | • effectelastin |
| • barkometer | • enzymes |
| • bateweight | • extract |
| • bisulfited | • fatliquoring |
| • chloride | • fibers |
| • chrome-tanned | • fixation |
| • chromic oxide | • grade |
| • collagen | • hair |
| • delimiting | • lime liquors |

I challenge you to shift your own paradigms of technical terms and innovations to drive more mutual understanding of the value they create to people and organizations.

Many companies do an excellent job of branding innovations. In our industry we could be more sensitive to branding, to drive market understanding of what these technologies do for the industry.

If there is one additional thing all companies in this space can do, it is to use marketing and social media to advance the cause of Leather and Chemistry Innovations.

Consider brand names used by chemical manufacturers. The names, colors, and symbolism. It's not a chemical compound composition, it's brand positioning.

When you see the words ECO, New Vero, Bio, Neo, Evo - you see words that are all indicative of support of this continued march towards sustainability and it's not only positioning from a brand, but also celebrating achievements in that area as well.

Let us talk about waste and waste elimination. Lean Manufacturing, I call The Lean Enterprise, derived from the Toyota Production System, is all about elimination of waste in the value stream. Lean practices and tools are open source. Any company can use what is out there. The key to a Lean Enterprise is not in the materials and tools of lean, it is the effectiveness of implementation of these tools.

My premise is that Sustainability is the same thing as the 7 wastes of production. The Lean concept of waste is that in the value stream of producing the product, there are losses in efficiency that can be eliminated if you are able "to see" them. They are categorized as:-

- Material Movement
- Inventory
- Waiting Time for material flow
- Defects in the process
- Producing more than needed at one time
- Man moves that are excessive
- Doing too much to the product

What is interesting is if you look at the papers that were written and presented to this ALCA conference, we see the number of papers that have to do with sustainability and waste.

I am not sure they were the same topics in Wilson's time, but it sure shows that we're right in tune with sustainability. We're right in tune with waste elimination.

And now a discussion around Lean and the 7 wastes and Sustainability. The lack of Sustainable products and Carbon foot reductions in plant operations should be considered as a form of waste. As continuous improvement engineers work to eliminate waste, we need to change our paradigm of sustainability as a form of waste to eliminate, hence the 8th waste

Our organizations need to implement metrics around the 8th waste to incentivize designers of products, facility and equipment engineers, plant managers to continuously drive the elimination of costs in product and process that makes us less sustainable. It's not just altruistic that we look at economic interests. It's not just because it feels good. It's not just because it seems to be the popular thing. Reducing waste is a terrific business proposition.

The business proposition is if you reduce waste, it's a cost reduction and a reduction the external costs we are exacting onto our world of limited resources (energy, people, material).

To conclude the conversation about Sustainability, it makes business sense to do it, and it drives our industry into a stronger narrative about our product globally. In Automotive Leather, competitors are among the most environmentally sensitive companies in the world. We are not the tanneries of 100 years ago. We are conscious, and we care. I am convinced that all the leather industries in different markets care as much about our environment as automotive does.

One of the goals of coming out of this paper, and at Pangea, is: part of our work is to publicize our efforts and take credit where credit is due.

Technical people can also drive the narrative of our product to increase demand. Synthetics are here to stay based on their cost proposition. We, as leather professionals, should not be okay with those products being called, either directly or implied, 'Leather' and letting a consumer think it is.

Europe has done the best job of driving regulation surrounding the use of Leather and spin-offs of the term. Legislation in some European countries is supporting the Leather description and banning the misuse of the term. Austria, Belgium, France, Italy and Lithuania, Portugal, Spain now prohibits using the word "leather" in non-leather applications and trade. In Italy, certain labelling is required on shoes describing what material is in the upper, sole, and lining.

Affiliated meat and hide associations are working on the same project in the United States to add labeling regulations in Washington DC.

Current US FTC Regulations have documented guidelines for Leather, but they omit Auto, furniture and clothing. There is much work still to be done, and there is a major effort to get these changed in the US to follow suit for what is happening in Europe. There are also similar efforts in industry groups in Asia.

The foundation of this regulation is already well done to reference cow hides as leather, it just needs to be driven into the rest of the industries that must follow. Deception is a tricky thing to prove unless it is outright done. Ignorance is deception, but harder to call it such. Therefore, consumer education is needed. To maintain an industry, we care so deeply about, we must drive innovation in product development and sustainability

We need to continue to provide a place for technical people to share their innovations and ALCA is a critical link in the chain of our

industry. Just as importantly, the ALCA needs to take the lead in helping our technical innovations in the industry and challenge our members to add a responsibility to promote them.

Challenge your companies to take your work and find a venue to promote it for the good of the industry.

Our story is a good one. The story we've got is more than powerful. It's compelling. Using another quote from Wilson's book, "When the history of progress is written, it will be found that the leather industry ranks high in its fundamental contributions to knowledge"

When Toyota welcomed the US manufacturers to learn about the Toyota Production System, they enriched themselves and the entire automotive industry. They gave it away.

That's what you need to do. Give it away and make the industry stronger. Seth Godin, in his book "Lynchpin" posits that the more of your knowledge and wisdom you give away, the more indispensable you become. As an industry, we need to become indispensable.

Social Media has a bad name for technical people like us. Marketing feels fake sometimes. The 4 big industries of Shoes, Furniture, Automotive, Apparel by themselves are a small industry of customers and professionals within those industries. Let me speak

about the Auto space as it relates to connecting with our customers about innovations and leather truthfulness.

Let say there are 30 significant automotive OEMs across the world. Within those companies, there are 20 or so major influencers of decisions whom drive product planners to specify leather or alternative material. Doing the math, that means there are 600 people in the world that strongly influence leather specifications. Double it and call it 1000 or even 2000.

Now look at how many of you are connected to a few of those influencers. Imaging if every one of you had the data, innovations, sustainability stories, and connected your information to these 2000 thought leaders. One of you know a dozen of these leaders. If everyone connected on their network and their networks network, imaging the influence and truthfulness we could get to those thought leaders. This is the power of Social and as technical leaders of the leather industry, this is your platform to drive innovation and truthfulness.

We don't need to go negative on synthetics, our product speaks for itself in performance. But our product does not speak as well as our opponents speak negatively about us. Find your Social voice to promote innovation and truth.



116th ALCA Annual Convention

June 21-24, 2022

Eaglewood Resort & Spa

Itasca, Illinois, USA

Technical Program starting Wednesday, June 22

John Arthur Wilson Memorial Lecture *"The Road Ahead"*

by Randy Johnson, President and CEO of Pangea Made, Inc., Rochester Hills, Michigan

Other Papers to be Presented on Wednesday and Thursday:

Climate Change Mitigation - How the Chemical Industry is Aligning to the Paris Climate Agreement
by Michael Costello, Stahl Holdings, Spain

Zeology, The New Standard in Tanning by Robert Doidge and Pim Wilgenburg,
Smit & Zoon Group, The Netherlands

Novel Enzymatic Beamhouse Processes as the Basis for Enhanced Organic Pre-Tanning Technologies by
Christopher Henzel, TFL Ledertechnik GmbH, Koln, Germany

The Future of ESG Reporting - Impacts and Opportunities for the Leather Industry by Kathryn Kutskill,
Sustainable Leather Foundation, UK

Optimization of a Zeolite Tanning Process by Manuel Navarro, Cromogenia Units, Mexico

Recovery of Industrially Useful Hair and Fat from Enzymatic Unhairing of Goatskins during Leather Processing
by Joseph Ondari Nyakundi, Leather Research Laboratory, University of Cincinnati, Cincinnati, OH

New Through Feed Fleshing Machine by Marc Oomens, im innovating, The Netherlands

Automotive Leather - An Insider Perspective on Material Testing by Roger Pinto, Pangea, Rochester Hills, MI

A Retrospective of Key Silicone Functionalities Which Contribute to Leather Manufacturing by Tim Roggow,
The Dow Chemical Company, Midland, MI

Science Based Environmental Footprint Reduction Strategies by Kim Sena, JBS Couros, Brazil

Materials Emissions Test Methods In The Automotive Landscape by Kevin Smith,
Eagle Ottawa by Lear, Rochester Hills, MI

Leather's Current Challenges and Opportunities by Stephen Sothmann,
Leather and Hide Council of America (LHCA), Washington, D.C.

COMELZ CNC Cutting Systems by Giulio Tandura, COMELZ, Italy

New Chrome Recovery Cleaning Technologies by Gerardo Villarreal, Semler Industries, Chicago, IL
and Jose Luis Gallegos Garcia, Elementis LTP, Milwaukee, WI

H.E.A.T. A New Sustainable Green Solution for Treating and Evaporating Hide Brine Wastewater by Russell Vreeland,
Eastern Shore Microbes, Belle Haven, VA

The Leather Image and the LN Modern Leather Guide by Luis Zugno, Leather Naturally, Memphis, TN

Presentation of the 2022 Fred O’Flaherty Service Award

by **John Rodden**

The Fred O’Flaherty award was created back in 1974 to honor those who have contributed and worked hard for the association over a period of years. The committee member for this year were: Sarah Drayna (chair), John Rodden and Katie Kutskill

The recipient of the 2022 Fred O’Flaherty Service Award has been an ALCA member since 1987 and began his leather apprenticeship during high school in 1976 at Hoyt & Worthen Tanning Corporation in Haverhill, MA. He completed his apprenticeship with one year at the sister company Cuir Hawtan SA, Port-au-Prince, Haiti along with completing the Corium Correspondence Course. In 1983 he graduated from the West German Tanning School in Reutlingen along with getting West German certification as tanner and master tanner. After graduation he returned to the Hoyt & Worthen group working both in the US and Haiti in various roles throughout the tannery and support functions. In 1990 he joined BASF as a Senior Sales Representative supporting a wide range of leather manufacturers in both wet-end and finishing. In 2005 he joined Eagle Ottawa LLC’s Product Development group working in R&D and technical support roles.

He has served as ALCA Councilor twice from 2009 to 2012 and again from 2015 to 2016. In 2016 he was elected to Vice President and served in that role until 2018. From 2018 to present he served as President of the ALCA.

It is truly an honor for me to present the 2022 Fred O’Flaherty Service Award to Michael Bley!



John Rodden presenting the Fred O’Flaherty Award to Michael Bley

Closing Address for the 116th Annual Convention

Michael Bley—

I want to give special thanks to our sponsors, who were able to let the 2020 sponsorship ride, and sponsored again for 2022. I want to thank Carol for acquiring two PPP loans, which were converted to grants. Thanks also to Steve who was able to significantly reduce our editing costs of the Journal. Thanks also to our advertiser and renewing members for their continued support. All of these contributions have helped us keep our doors open the last two years.

Now, we have to look to the future. Many people may not realize it, but there is a lot of volunteer work going on behind the scenes to make this Association and Convention a success. The Association, your Association, needs your support in these functions. From the beginning, before any of us volunteered, we did not know how to fulfill all of the tasks involved. But I have found, that previous members who have done the same role and Carol are always will to guide you. Again, the Association, your Association needs your support in order to stay strong and viable. So I ask you if you are asked to volunteer, give it a second thought. If you are ambitious, and want to volunteer before being asked, just let one of the Officers or Carol know. With new volunteers comes new ideas and new ideas are what we need to move forward.

And now it is time for me to end my six year VP/P term and pass the gavel to the new President of the ALCA, Joseph Hoefler! I have great confidence; he will serve the Association very well as will John Rodden.

Thank you!

Joseph Hoefler—

Good evening to my esteemed ALCA colleagues. I want to first thank you all for attending and especially recognize the presenters and organizers for making this event such a wonderful experience. After so much time has passed without getting together due to Covid, missing two consecutive conventions, these past few days were like a reunion of sorts, akin to meeting distant family members, because ALCA is just that a family. Additionally at this time I would like to further acknowledge Carol as the matriarch of this family because without her I doubt that the Association or Convention could come close to what it has been.

I appreciate the responsibility and confidence placed in me and will strive to live up to expectations and hopefully follow in the footsteps of successful past presidents, like Mike, who set a great example to emulate. The ALCA Council have our work cut out for us and will need to begin to do so in the immediate future as we have Carol's replacement to consider, the next convention to plan, and of course another technical paper session to begin to solicit support for, no doubt the new Vice President John Rodden will do a fine job with his responsibility.

In closing let's enjoy the remaining time we have left together as we will go our separate ways soon after but shortly after lets also begin to think about the future and how we can make the most of things to come!

Take care, safe travels, and good night.



Michael Bley passing the gavel on to Joseph Hoefler

Council Meeting Minutes

AMERICAN LEATHER CHEMISTS ASSOCIATION

Eaglewood Resort & Spa, Itaca, IL

June 21, 2022

Officers: Mike Bley, Joseph Hoefler
 Councilors: Jose Gallegos, Steve Lange, Lee Lehman and John Rodden
 Executive Secretary: Carol Adcock

1. WELCOME – Mike Bley, President

President Mike Bley called the meeting to order and welcomed everyone. President Bley reported that the Wilson Speaker, Randy Johnson, is leaving prior to the banquet. He therefore suggested that Mr. Johnson be presented the Wilson Scroll after his presentation. Eric Webb will introduce Mr. Johnson as well as give him the scroll after his presentation.

Results from electionbuddy.com were announced. The Association's new Vice President will be John Rodden. New councilors will be Myron Hooks and Roger A. Pinto. Mrs. Adcock announced that 75 votes were cast out of the 202 ballots sent out which is 37%. This was a little lower than the average amount of votes cast in the past.

2. OLD BUSINESS – Mike Bley, President

LIFE MEMBER

There were four candidates for life membership in the Association, namely Boghos Assadourian, Gian Franco Grandi, Visvanathan Prasanna and Blane Shoemake. Bio of Gian Franco Grandi was previously emailed to Council. Mrs. Adcock reported that the Association has no contact information for Mr. Prasanna. In view of being unable to reach him by email, Council decided to put his record in the Association's delete database until such time that contact can be found.

The criteria for life status in the Association is that the member has been a paying member or paying and then retired member of the Association for forty (40) years. Motion was made and seconded and unanimously passed to give Boghos Assadourian, Gian Franco Grandi and Blane Shoemake life status in the Association.

3. CONVENTION ITEMS AND REVIEW OF CONVENTION – Bill Clippinger

Since Mr. Clippinger was unable to attend the convention due to illness, he had asked Sarah Drayna to fill in. She agreed but was also unable to attend due to illness at the last minute. Therefore, Mrs. Adcock reviewed the overall schedule for the convention with Council. Mrs. Adcock said there was one change on the schedule. It was for the start of the Fun Run. The new starting time was to be 5:00 pm in order to give people more time to change before the cocktail reception and dinner. She also reviewed the rooms for each event but did not tour them as most of Council was present at the 2018 convention at Eaglewood and knew where the rooms were located. Since no one from the hotel had shown up for the meeting, Mrs. Adcock emailed the hotel representative, Matt Forsythe, and he then came to the meeting. There as concern over the kitchen closing early on Wednesday night when the group would be at Kegler's. Mr. Forsythe assured Council that the kitchen would stay open until 9 pm and was scheduled to put out hot food at that time. Mrs. Drayna has previously ordered the food for Kegler's as well as reviewed all meals planned for the convention.

4. EDITOR'S REPORT – Steve Lange

Mr. Lange submitted the following written report dated June 12, 2022:

We are on track to publish 50 papers in 2022. Confirmed manuscripts are scheduled through November. I do not have any of the papers intended to be presented at the 2022 Convention (two of the presentations have already been published in the Journal). Four papers have been rejected in 2022.

The online version of the Journal dates to January 2007. The Top Ten Abstract and Article views are summarized on the next page for that time period.

I have been working with UC Press to get older editions of the Journal published online. Based on their suggestion, I am working back from 2007. So far, 2000 to 2006 have been scanned and currently working on the 1990 issues. The older issues are being scanned as searchable PDF files and will, hopefully, be uploaded soon.

Respectfully submitted,
Steve Lange
Journal Editor

Discussion was held regarding the Editor's Report. Mr. Lange said he had not received invoices for printing the Journal since October of 2021. He had asked for them on numerous occasions, but none had been received. He reviewed the JALCA Website Analytics with Council. It was felt that the statistics about how many people were viewing the Journal would be good for getting companies to advertise in the Journal. President Bley reported that Mr. Lange's original contract had expired and he has agreed to renew his contract for a period of five years.

Motion was made, seconded, and carried to accept the Editor's Report as written.

JALCA WEBSITE ANALYTICS
January 2007 to June 2022

Table 1 TOP TEN ABSTRACT VIEWS

Article Title	Date Published	Abstract Views
A Future for Leather!	7/1/2019	2102
Comparison of the Sustainability of the Vegetable, Wet-White and Chromium Tanning Processes through the Life Cycle Analysis	3/23/2020	513
Eco-friendly Leather Dyeing using Ultrasound Technique	6/1/2020	505
Country-level Life Cycle Assessment of Carbon Footprint in Processing of Bovine Upper Leather	6/1/2019	471
Machine Vision Inspection System for Detection of Leather Surface Defects	1/1/2019	470
Investigation of the Interaction between Epoxides and Collagen in Epoxy Tanning based on BDDGE Cross-linked Collagen Solution	8/3/2020	451
A Novel Approach for Lightfast Wet-white Leather Manufacture Based on Sulfone Syntan-aluminum Tanning Agent Combination Tannage	6/1/2018	446
The Effect of Palm Oil Sulfatation Time on Fatliquor Quality and Finished Leather Product	5/1/2020	418
Treatment And Valorization of Leather Industry Solid Wastes: A Review	2/1/2009	358
Preparation and Properties of Thermally Expandable Microspheres for Foam Coating	9/7/2021	357

Table 2 TOP TEN WHOLE ARTICLE VIEWS

Article Title	Date Published	Total PDF Views
Enzymes in the Leather Industry, a special review paper	4/1/2013	960
Chemistry of Syntans and Their Influence on Leather Quality	11/1/2015	924
Nanotechnologies for Leather Manufacturing: A Review	8/1/2011	739
Short-term Preservation of Hide and Skins Using Peracetic Acid	1/1/2016	709
Preparation of Formaldehyde-free Melamine Resin using Furfural as Condensation Agent and its Retanning Performances Investigation	6/1/2018	621
Damage of Pickled Hides, Wet-blue Leather and Vegetable Tanned Leather Due to Biodeterioration	5/1/2015	554
Sodium Chloride Substitute for Lower Salt Goat Skin Preservation: A Novel Approach	8/1/2017	495
Collagen Hydrolysate Extraction from Chromed Leather Waste for Polymeric Film Production	1/1/2016	458
Reaction of Protein and Carbohydrates with EDC for Making Unique Biomaterials	4/1/2016	426
Anaerobic Digestion of Leather Industry Wastes - An Alternate Source of Energy	2/1/2017	393

5. FINANCIAL REPORT – Carol Adcock

The Council was sent the first quarter 2022 financials including the Profit and Loss Statement, Balance Sheet and Budget vs. Actual prior to the meeting.

The Membership and Subscription Report was also reviewed. The ALCA currently has 278 members consisting of 122 active, 43 active life, 4 active life mutual, 21 active life retired, 14 active mutual, 42 active retired, 28 SLTC, 3 SLTC students, and 1 ALCA student. It was noted that The Association had been notified that 16 members and/or friends of the leather industry had passed away since the last ALCA Annual Convention in 2019. A moment of silence will be held for all of them at the Annual Business Meeting. It was also noted that four members, Kadir Donmez, Richard Evans, Cheng-Kung Liu and Constantin Rosu, had been given retired status with the Association. Three members, Juan Hernandez, Timothy Howes, and John S. Moore, were given life status in the Association.

For 2022, 135 paying members contributed \$26,211. There is outstanding approximately \$1,399 in dues from the SLTC after subtracting the dues of our mutual members. Subscriptions for 2022 have brought in \$8,815 in fees and \$2,520 in postage and handling charges. Discounts have been given in the amount of \$604.50, making a total of subscriptions and postage and handling charges minus discounts in the amount of \$10,730.50. Twenty-six new members have joined ALCA since the last Annual Convention: twenty-one active members, two SLTC student members, and three SLTC members.

Motion was made, seconded and passed to accept the Financial Report as presented.

Mrs. Adcock reported that the Association's Financial Analysis had been completed and is attached to these minutes. She also told Council that she had originally wanted to retire at the end of 2022 but has decided to continue at least through another convention in view of the fact that the Association would be celebrating its 120th anniversary.

6. WAYS AND MEANS COMMITTEE – Shawn Brown and Steve Schroeder, Jr., Co-Chairs

Shawn Brown, Co-Chair for the Ways and Means Committee, submitted a written report for the Annual Business Meeting. Mrs. Adcock gave the following numbers on the investment account:

First Quarter 2022 earnings - \$573.43 compared to first quarter of 2021 of \$757.24; have not received any dividend checks from the company this year;

Value of Portfolio as of March 31, 2022 - \$179,830.68; was \$208,559.95 end of March 2021;

Withdrawals in 2021 were \$24,000 received on 8/10/2021 and \$20,000 received on 9/10/2021.

The term of the Co-Chairs had expired. Both have agreed to serve another two years.

Motion was made, seconded and carried to accept the Ways & Means Committee Report.

7. ANNUAL CONVENTION

2023 Annual Convention

Council discussed the fact that the Association would be 120 year old next year. It was felt that the 117th Annual ALCA Convention should celebrate that fact. It was felt that as many past presidents in attendance would be a nice way to celebrate. Discussions had been held previously regarding the inclusion of the Leather and Hide Council of America (LHCA) within the Association's 117th Annual Meeting. Council called Mrs. Drayna for her input. She was asked to pursue sites for the 2023 convention and to visit with Stephen Sothmann of the LHCA to see if there was a way to incorporate their meeting with the Association's convention. She agreed to pursue these matters.

8. COMMITTEE APPOINTMENTS– Mike Bley, President

President Bley announced his recommendations for the following appointments:

2023 Nominating Committee: Mike Bley (Chair), Steve Lange, John Rodden

2023 ALSOP Committee: Joseph Hoefler (Chair), Mike Bley, Luis Zugno

2023 O’Flaherty Award Committee: Sarah Drayna (Chair), Mike Bley, John Rodden

2024 Wilson Selection Committee: Jeff Miller (Chair), Eric Webb, Katie Kutskill

Motion was made, seconded, and carried to accept the appointments as presented.

9. NEW BUSINESS– Mike Bley, President

New business to come before Council was the retirement of Mrs. Adcock, Executive Secretary. Mrs. Adcock said she felt it might be best to do something similar to what happened when she took the position and ask the Council as well as the membership if there was a company willing to house the Association’s business office. Another idea would be a member of the Association taking over the position. Council will be working on this during the company year. Mrs. Adcock was asked to prepare a job description which she will do.

11. ADJOURNMENT

The next Council meeting will be Thursday, June 23, at 8 am in the Hickory Board Room. It will be a short meeting before the technical sessions begin for the day including the current Council as well as the new members of Council.

There being no further business, the meeting was adjourned.

Respectfully Submitted by:

Carol Adcock, Executive Secretary



SCOTT NORTHAM, CPA, PC
Certified Public Accountants

INDEPENDENT ACCOUNTANT'S REPORT ON APPLYING AGREED-UPON PROCEDURES

American Leather Chemists Association
1314 50th Street, Suite 103
Lubbock, TX 79412

We have performed the procedures enumerated below, which were agreed to by American Leather Chemists Association (ALCA), solely to assist you in evaluating the revenue and expense transactions of the Organization for the fiscal year ended December 31, 2021. ALCA's management is responsible for the presentation of the revenue and expense transactions. This agreed-upon procedures engagement was conducted in accordance with standards established by the American Institute of Certified Public Accountants. The sufficiency of these procedures is solely the responsibility of those parties specified in this report. Consequently, we make no representation regarding the sufficiency of the procedures described below either for the purpose for which this report has been requested or for any other purpose.

We examined the detailed general ledger and a representative sample of the revenue and expense transactions and the related underlying supporting documentation for the organization for the fiscal year ended December 31, 2021 for the purpose of determining whether the documentation presented properly supported the revenue and expense transactions and were properly categorized within the financial records. We found no significant exceptions within the revenue and expense transactions tested.

We were not engaged to conduct, and did not conduct, an examination, the objective of which would be the expression of an opinion on the financial statements of the Organization. Accordingly, we do not express such an opinion. Had we performed additional procedures, other matters might have come to my attention that would have been reported to you.

This report is intended solely for the information and use of by the directors and management of American Leather Chemists Association and is not intended to be and should not be used by anyone other than those specified parties.

SCOTT NORTHAM, CPA, PC
Ruidoso, New Mexico
March 24, 2022

1035 Mechem Drive
Ruidoso, NM 88345

(575) 258-5559
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AMERICAN LEATHER CHEMISTS ASSOCIATION

Annual Business Meeting

116th Annual Convention

Eaglewood Resort & Spa, Itasca, IL

June 23, 2022

President Mike Bley welcomed Officers, Councilors and Members and called to order the annual business meeting of the 116th Annual Convention of the American Leather Chemists Association.

1. NEW MEMBERS:

A warm welcome was extended to the 23 new active members who joined the association during the past three years along with 5 new SLTC members. Mrs. Adcock asked all new members present to stand. There were several new members present at the convention. Congratulations were extended to 3 members, Boghos Assadourian, Gian Franco Grandi and Blane Shoemake, who had met the requirements and were approved for life status with the Association and to four members, Kadir Donmez, Richard Evans, Cheng-Kung Liu and Constantin Rosu, who received retired status in the Association.

2. OFFICERS AND COUNCIL**a. Officers Continue:**

At the end of the convention, Joseph Hoefler moves to President and John Rodden becomes Vice President.

b. Council Changes and Presentation of Certificates:

Retiring councilors Jose Luis Gallegos and John Rodden were thanked for their service and contributions during the past five years. Both were presented with a certificate. The results of the election were announced and the incoming councilors for 2022-2025 will be Myron Hooks of Dow Chemical Co. and Roger A. Pinto of Pangea Made, Inc. The new councilors were congratulated, and appreciation was extended to the Nominating Committee, John Rodden, Chair, Joe Hoefler and Katie Kutskill, for their service to the Association.

3. COMMITTEE APPOINTMENTS:

The By-Laws state: "The composition of the Nominating Committee shall be reported to the membership at the annual meeting, and shall be subject to ratification by the active members there present." This motion was made at the Business meeting and the following members of the 2023 Nominating Committee were approved:

Mike Bley (Chair), Steve Lange and John Rodden.

The following appointments approved by Council were announced:

2023 O'Flaherty Service Award Committee: Sarah Drayna (Chair), Mike Bley and John Rodden

2023 Alsop Award Committee: Joseph Hoefler (Chair), Mike Bley and Luis Zugno

2024 Wilson Memorial Lecture Committee: Jeff Miller (Chair), Eric Webb and Katie Kutskill

Andreas Rhein of Tyson Foods agreed to continue as the Association's IULTCS representative for the next three years.

4. EDITOR'S REPORT: Steven D. Lange

Mr. Lange gave the following report:

We are on track to publish 50 papers in 2022.

Confirmed manuscripts are scheduled through November.

Two papers from the 2022 Convention have already been published.

I do not have any of the other papers presented at the 2022 Convention.

Four papers have been rejected in 2022.

The online version of the Journal dates to January 2007.

The Top Ten Abstract and Article views were summarized in table format and were the same as shown previously at the Council meeting. It is interesting that the abstract and article view lists do not overlap.

I have been working with UC Press to get older editions of the Journal published online. Based on their suggestion, I am working back from 2007. So far, 2000 to 2006 have been scanned and currently working on the 1990 issues. The older issues are being scanned as searchable PDF files and will, hopefully, be uploaded soon.

Respectfully submitted,
Steven D. Lange
Journal Editor

5. STATE OF THE ASSOCIATION:

a. Membership Review:

A total membership of 278 members, of whom 135 are paying members, was announced. It was noted that the chart showed the paying membership to be slightly increasing which was good.

b. Convention Account:

A bar chart was shown indicating the income and expenses for the annual conventions since 2013. The chart reflected revenue of \$64,475, expenses of \$32,584 for a profit for 2019 of \$32,891.

c. Convention Attendees:

A review of the attendance for 2019 revealed that 17 tanners representing 12 tanning companies, 51 suppliers representing 17 individual chemical companies and 9 individual equipment companies, and 2 research scientists/trade organizations representing 2 organizations were present. Other attendees included 2 ALCA staff, 1 press, 3 consultants, and 1 guest for a grand total of 76.

d. Investments:

The Ways & Means Committee continues to be co-chaired by Shawn Brown and Steve Schroder, Jr. The year to date figures were given for the investment account showing a change in value from \$198,875.08 to \$169,668.57. The loss was indicative of the market in general right now.

e. Sponsorship: This year's meeting had the same sponsorship campaign that was used in 2019. Under this program, there are seven levels of sponsorship, namely, Bronze, Silver, Gold, Diamond, Platinum, Elite 1 and Elite 2. This year we had 1 Elite 2, 3 Platinum, 3 Diamond, 3 Gold, 2 Silver, and 6 Bronze donors. A list of the specific sponsors for each category was shown. The association is very indebted to the generosity of all the sponsors.

6. NEW BUSINESS:

a. Website info:

Everyone was reminded to go to the Association's website at www.leatherchemists.org for information about the Association as well as updates on next year's convention as they develop.

b. 2023 Annual Convention:

The Association will name the site of the 117th Annual Convention at a later date, but it will be a celebration of 120 years since the Association was founded.

7. 2023 WILSON LECTURE:

The 2023 Wilson Lecturer was announced. It will be Mike Redwood of Leather Naturally, teacher at University of Bath School of Management, and Trustee of the U.K. Leather Conservation Centre. His bio was given and will be posted on the Association's website under Annual Convention/Wilson Lecture.

Appreciation was given to the 2023 Wilson Selection Committee, Jeff Miller (Chair), Eric Webb and Doug Morrison for their work in selecting a lecturer.

8. IN MEMORY:

There was a moment of silence observed for members and friends in the leather industry who passed since our last convention:

Philip L. Baxter	March 15, 2019
Hubert M. Wachsmann	May 25, 2019
Eduardo V. Diharce	November 2, 2019
Thomas William Krisko	August 9, 2020
Rodney Hammond	August 13, 2020
Henry Walter Koelblinger	December 10, 2020
Raymond A. Hart	March 30, 2021
Guy H. Moberg	May 2, 2021
Leo Devarenne	June 6, 2021
Thomas P. Mulherin	June 16, 2021
David Rabinovich	July 1, 2021
Bruce A. Rittel	Sept. 21, 2021
Martin P. Heise	December 9, 2021
Robert A. Denbow	February 14, 2022
Thomas Emmerling	Sept. 14, 2021
Thomas Bley	March 24, 2022

11. ADJOURNMENT:

President Mike Bley called for a motion to adjourn the annual business meeting held at the 116th convention of the American Leather Chemists Association. The motion was made and seconded. Motion carried.

Council Meeting Minutes

AMERICAN LEATHER CHEMISTS ASSOCIATION

Eaglewood Resort & Spa, Itaca, IL

June 23, 2022

Officers: Mike Bley, Joseph Hoefler
Councilors: Jose Gallegos, Steve Lange and John Rodden
New Councilors: Myron Hooks and Roger Pinto
Executive Secretary: Carol Adcock
Guest: Stephen Sothmann

1. WELCOME – Mike Bley, President

President Mike Bley called the meeting to order and welcomed everyone. New Vice President John Rodden and new Councilors Myron Hooks and Roger Pinto were welcomed. Thanks were extended to outgoing Councilors Jose Gallegos and John Rodden.

2. COMMENTS ON CONVENTION – Mike Bley

President Bley asked for feedback from the convention. It was felt that the technical session room was one of the best and that breaks were very good. Everyone thought the bowling and activities night was an excellent way for people to get to know each other and network. It was suggested that we try to have an activity night each year to help new people to get to know everyone. It was felt that next year first time convention attendees could have some sort of identification on their badge so Council could make sure they introduced themselves to first time attendees.

3. COMMENTS REGARDING DUTIES OF NEW COUNCILORS

Mrs. Adcock explained to the new councilors that most of their duties involved replying to email votes on new members and other items needing approval by Council. She explained that the Council was compiled of two officers, namely President and Vice President, and six councilors. The officers serve for a two year term while the councilors serve for a three year term. It was pointed out that another very important part of the duties of the councilors was to support and help the Vice President get speakers for next year's convention. After the meeting the new councilors were sent their job description along with first quarter financials, guidelines for the Alsop Award, the O'Flaherty Award, the Wilson speaker, the Lollar Prize Paper, the Rowles Scholarship and a new Council contact list. The officers were also sent such items after the convention.

4. ISSUES FROM PRIOR COUNCIL MEETING

Stephen Sothmann was asked to talk about his ideas for having the Leather and Hide Council of America (LHCA) meeting alongside the 117th ALCA Annual Convention. He said that his group had two meetings per year, one in DC in April and the other in October in Chicago. The average attendance at the April meeting was 30, and the average attendance of the October meeting was 70. The meeting was one and a half days. It was felt that this idea was worth pursuing and might help boost attendance and sponsors for the ALCA. Mr. Sothmann said his parent organization had expertise and could help explore sites for the combined meeting. He and Mrs. Drayna will be meeting about a format for such a meeting and how it would work.

5. WRAP UP/NEXT COUNCIL MEETING

The next Council meeting will be in October. A date will be set later.

6. ADJOURNMENT

Since it was time to get to the technical sessions, the meeting was adjourned.

Respectfully Submitted by:
Carol Adcock, Executive Secretary

Synthesis and Retanning Performance of a Novel Melamine Resin with Ultralow Formaldehyde Content

by

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Abstract

Diethanolamine, epichlorohydrin (ECH), and lysine were used to change the traditional synthesis route to address the formaldehyde emission issue of melamine resin (MR), and a novel waterborne MR retanning agent with ultralow formaldehyde content (MUF) was finally obtained. The structure of MUF was characterized by Fourier transform infrared spectroscopy, ¹³C nuclear magnetic resonance, and X-ray photoelectron spectroscopy, and its retanning performances in wet-blue and wet-white leathers were thoroughly investigated. Results showed that the formaldehyde content of MUF was 28.05 mg/kg, which was greatly lower than that of traditional MR (3550.23/2543.45 mg/kg), and the formaldehyde contents of chrome- and TWLZ-tanned leathers retanned by MUF were only 12.68 and 8.98 mg/kg, respectively. The thickening rates of MUF-retanned leather were up to 13.40% (chrome-tanned leather) and 9.58% (TWLZ-tanned leather), and MUF showed a satisfying overall performance in retanning leather. MUF is highly promising in practical application owing to its ultralow formaldehyde content, excellent stability in aqueous solution, and satisfactory retanning behaviors.

Introduction

Melamine resin (MR) has high filling and coordination ability in the leather retanning process, but the formaldehyde emission issue has limited its further application.¹ Formaldehyde is a proven carcinogen; inhaling it may have chronic effects, such as shortened lifespan, reproductive problems, and lower fertility.² Many countries have set standards for formaldehyde content in leather, and this restriction is becoming increasingly stringent.³⁻⁴

The common approach to decreasing the formaldehyde content in MR is to reduce the molar ratio of formaldehyde/melamine in the synthesis process.⁵ However, the reduction of formaldehyde dosage definitely lowers the reactivity of the synthesis process and finally causes poor retanning performances. Other attempts

were also conducted, including optimizing synthesis parameters, adding formaldehyde scavengers, and replacing starting materials.⁶ Even these attempts are somewhat effective to reduce the formaldehyde content of MR, but the overall retanning performances and formaldehyde content in leather hardly meet the practical requirements.^{1, 6-7} Therefore, a novel MR with excellent retanning performances and ultralow formaldehyde content is still a challenge.

The traditional synthesis route should be changed to effectively solve the formaldehyde problem. Generally, the conventional synthesis route of MR includes two processes, hydroxymethylation and condensation (Figure 1), and the dosage of formaldehyde is often excess to ensure the complete reaction of melamine.⁸ In the hydroxymethylation stage, formaldehyde was reacted with melamine to generate the intermediate product, methylmelamines, but this reaction is reversible (Figure 1b). Then, in the following condensation stage, the formerly generated methylmelamines will crosslink with each other and finally result in the formation of polymer resins (MR). Accordingly, formaldehyde residues in the MR have two main sources. First, a considerable amount of unreacted formaldehyde is formed in the hydroxymethylation process, the unreacted formaldehyde is the direct source of formaldehyde in MR.⁹ Second, the condensation stage is usually accompanied by the formation of methylene ether bonds (Figure 1c). Methylene ether bonds are unstable; they can break in certain conditions and finally lead to formaldehyde generation (Figure 1d).¹⁰ The breakage of methylene ether bonds is responsible for the continuous formaldehyde release of MR. Therefore, if the intermediate product of methylmelamines can be continuously consumed, the reaction extent of melamine and formaldehyde will accordingly increase, and the unreacted formaldehyde will be mostly reduced (Figures 1a-b). If the formation of methylene ether bonds can be avoided during the condensation process of methylmelamines (Figures 1c-d), the continuous formaldehyde generation and release problem of MR can also be well addressed.

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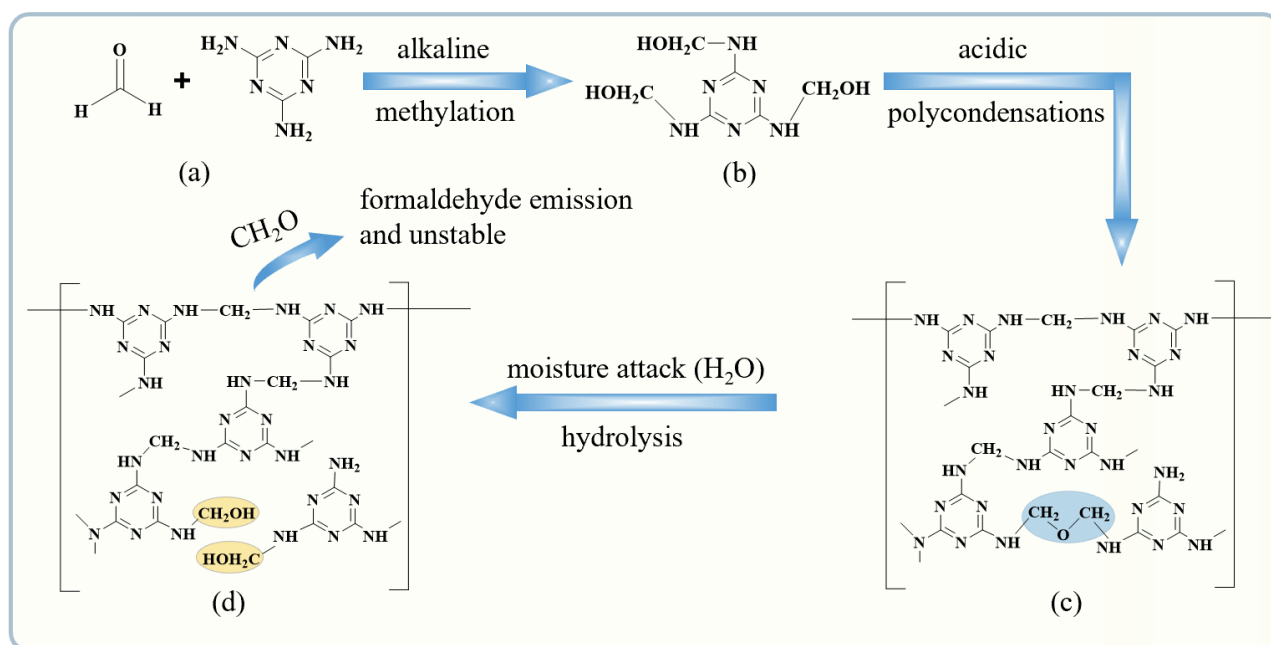


Figure 1. Synthesis process of traditional MR (a-c) and formaldehyde emission caused by the breakage of methylene ether bonds (d).

Therefore, the aim of this study was to develop a feasible and effective method for the synthesis of ultralow-formaldehyde MR. Here, diethanolamine, formaldehyde, and melamine were first reacted to prepare triazine ring-containing polyols (TRPs, Figures 2a-b). Through this approach, the reaction of formaldehyde and melamine can be completely performed, leading to a great decrease in unreacted formaldehyde. Then,

the prepared TRPs were further reacted with epichlorohydrin (ECH) to prepare the intermediate product of Chlor-containing intermediates (CCIs, Figure 2c). Finally, a condensation reaction (crosslinking) was initiated by lysine (Figure 2d), and a waterborne MR retanning agent with ultralow-formaldehyde content (MUF) was obtained.

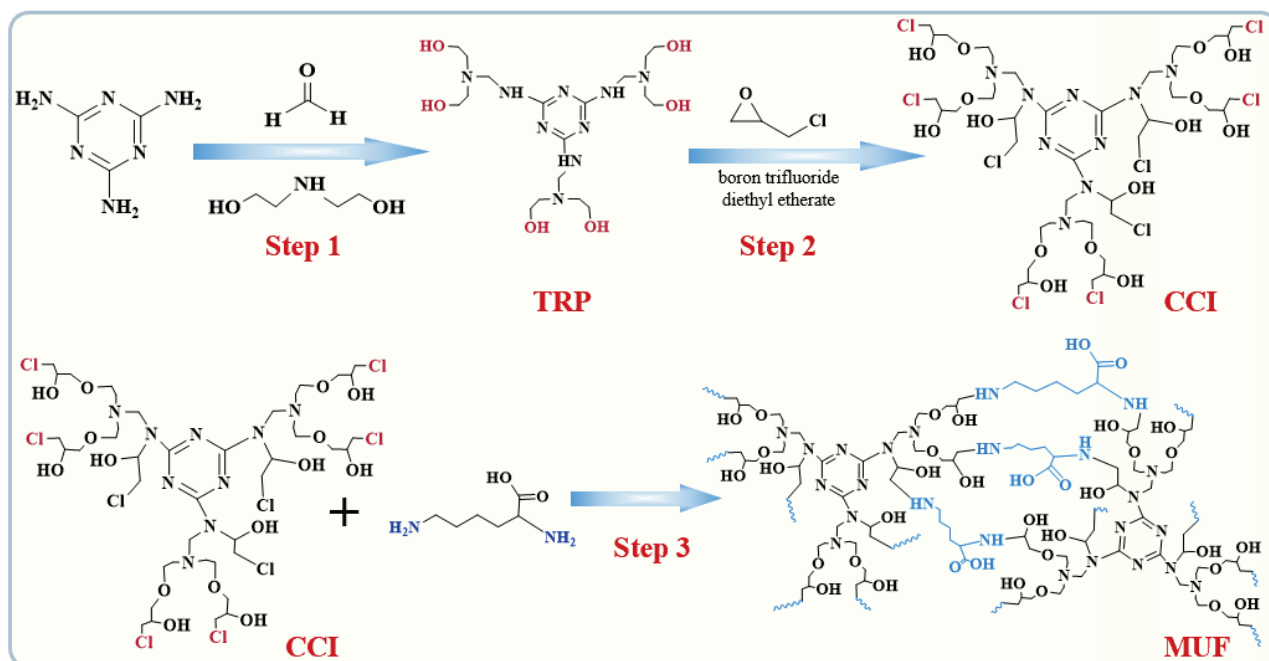


Figure 2. Schematic of the synthesis process of MUF.

Materials and Methods

Materials

Paraformaldehyde, diethanolamine, melamine, boron trifluoride diethyl etherate, acetone, sodium hydroxide and ECH were analytically pure and purchased from Chengdu Kelong Reagent Chemical Factory, China. Lysine was obtained from Shandong Usolf Chemical Technology Co., Ltd, China. Acetonitrile was chromatographically pure and purchased from Sigma-Aldrich Co., LLC, USA. Wet-blue and wet-white leathers were prepared by our laboratory. All other chemicals used for leather manufacturing were commercial grade. TWLZ, a commercial chrome-free tanning agent, was presented by Tingjiang New Materials Co., Ltd. (Sichuan, China).

MUF preparation

The MUF synthesis process is shown in Figure 2.

TRP synthesis

First, 315.42 g diethanolamine and 90 g paraformaldehyde were added into a 1000 mL three-neck round bottom flask with a mechanical stirrer. The three-neck flask was placed in an oil bath at 80°C, and the reaction was stirred for 1.5 h. Then, 126 g melamine was added to the flask for 6 h to prepare TRPs. The TRP was washed thrice with acetone and filtered to remove unreacted components, and the yield was 78.96%.

CCI preparation

The prepared TRP (24 g) and boron trifluoride diethyl etherate (0.7 g) were added to the three-neck flask and stirred for 5 min at room temperature. Thereafter, 45 g ECH was dripped into the above mixture within 30 min. Afterward, the temperature of the oil bath was increased to 60°C and held for 24 h. Finally, a clear and transparent CCI solution was obtained. The CCI was washed thrice with acetone and filtered to remove unreacted components, and the yield was 89.86%.

MUF synthesis

Lysine (8.22 g) was dissolved in 24.66 g water, and the solution was then transferred to a three-neck flask to react with 12.9 g CCI at 60°C for 2 h. Afterward, the temperature was increased to 90°C for further reaction for 2 h, and the mixture was kept in pH 9~10 conditions by 30% NaOH solution throughout the reaction. The MUF was purified by dialysis through dialysis tubing (MWCO, 500) for three days and freeze-dried.

Characterization of intermediate and final products

Fourier transform infrared (FTIR) spectroscopy analysis

TRP, CCI, and MUF were separately lyophilized, and FTIR spectroscopy (Nicolet IS10, Thermo Scientific, USA) was used to characterize their structures in the wave range of 400–4000 cm⁻¹ using compressed KBr pellets. The crust leathers retanned by MUF, CMS, CML, and control sample (without retanning) were trimmed into 2 cm×2 cm pieces to be tested using FTIR spectroscopy.

Nuclear magnetic resonance (NMR) spectroscopy

The ¹³C-NMR spectra of TRP, CCI, and MUF were recorded on a Bruker Advance II 400MHz NMR spectrometer (Bruker, Swiss). The solvent used for TRP and CCI was dimethyl sulfoxide (DMSO-d₆, 99.8 atom% D) containing 0.03% (v/v) tetramethylsilane (TMS), and the solvent for MUF was deuterium oxide (D₂O, 99.8 atom% D) because of their differences in solubility.

X-ray photoelectron spectroscopy (XPS) analysis

XPS elemental surface analysis was achieved through an X-ray photoelectron spectrometer (Thermo Fisher Nexsa, USA) with a monochromator Al K α X-ray source (1486.6 eV).

Storage stability and release of formaldehyde content during storage

The prepared products adjusted to pH 3.8/7.0 were stored at 80°C for 168 hours, which could accelerate the methylene ether bond breakage and molecular movement in the solution. During storage, the storage stability of the prepared products was assessed by observing the state of the solutions, and the formaldehyde contents were also determined by high-performance liquid chromatography (HPLC) according to ISO/TS 17226:2003. For comparison, a typical commercial liquid MR (CML) was also evaluated.

Particle size and isoelectric point (pI) analysis

The average particle size of the MUF solution (1 g/L) was determined by NanoBrook Omni (Brookhaven, USA). The pH of the MUF solution was adjusted to the pH gradient of 2–10 with 1 mol/L HNO₃ and 1 mol/L NaOH to further measure the pI of MUF. For comparison, two typical commercial melamine resins, CML and powder (CMS), were also investigated. CML is in the liquid form and has a higher degree of sulfonation, whereas CMS is in a powder form with a low degree of sulfonation.

Retanning performances of MUF

The retanning performances of MUF in wet-blue (chrome tanned) and wet-white leathers (TWLZ tanned) were investigated. The leather

Table I
Wet-blue retanning processes

Process	Chemicals	%	Duration (min)	Remarks
Rewetting	Water	250		
	Degreasing agent	0.3		
	Formic acid	0.5	60	pH≈3.2, Drain
Washing	Water	400	10	Drain
Chrome Retanning	Water	200		
	Chrome powder	4	90	
	Sodium formate	1	30	pH≈3.4
	Sodium bicarbonate	0.3	90	pH≈4.0, Drain
Neutralization	Water	200		
	Sodium formate	2	30	
	Neutralization tannins	2		
	Sodium bicarbonate	1	60	pH≈5.5, Drain
Washing	Water	400	10×2	Drain
Retanning	Water	100		
	MUF/CML/CMS	10	90	
Fatliquoring	Water	100		
	Fatliquoring agent	8	50	
	Formic acid	2	4×15	pH≈3.4
Washing	Water	400	10×3	Drain

Note: based on wet blue weight (w/w)

Table II
Wet-white retanning processes

Process	Chemicals	%	Duration (min)	Remarks
Rewetting	Water	400		
	Nonionic degreasing agent	0.5		
	Formic acid	0.3	40	
Neutralization	Water	200		
	Sodium formate	2		
	Neutralization tannins	3	30	
	Sodium bicarbonate	0.6×2	15×2+60	pH≈6.0, Drain
Washing	Water	400×2	10×2	Drain
Retanning	Water	100		
	Synthetic tanning agent	10	90	
	MUF/CML/CMS	10	120	Drain
Fatliquoring	Water	150		
	Fatliquoring agent	10	120	
	Formic acid	0.4×2	15×2	pH≈3.6
Washing	Water	200	15	Drain

Note: based on shaving leather weight (w/w)

samples were cut into halves through the backbone. The retanning processes are summarized in Tables I (wet-blue leather) and II (wet-white leather). It should be noted that TWLZ is a kind of aluminum-zirconium combination tanning agent, and the isoelectric point of TWLZ leathers is higher than that of wet blue tanned by chrome tanning agent. As a result, in the retanning process of TWLZ, the neutralization pH of TWLZ tanning is set higher than chrome tanning to maintain an appropriate gap between bath pH and TWLZ leather isoelectric point, which can avoid leather from the excessive surface combination. For comparison, the two commercial MR agents (CML and CMS) were also investigated as the control samples.

Absorption of retanning and fatliquoring agents

The effluents before and after the retanning/fatliquoring process were individually collected to measure the absorption of retanning/fatliquoring agents based on total organic carbon (TOC) concentration (Elementar, Germany). The absorption rates of the retanning agents were calculated using Equation (1):

$$\text{Absorption rates} = \frac{(T_1 - T_2)}{T_1} \times 100\% \quad (1)$$

where T_1 and T_2 are the TOC values of the bath collected at the beginning and ending of retanning/fatliquoring, respectively.

Thickening rates of retanned leather

The average thickness of the leather samples were measured by a dial thickness gauge (MingYu, China), and thickness rate (R) was calculated as follows:

$$R = \frac{(S_2 - S_1)}{S_1} \times 100\% \quad (2)$$

where S_1 and S_2 are the average thicknesses of the leather samples before and after retanning, respectively.

Physical and mechanical strength of leather

All samples were kept at $25 \pm 2^\circ\text{C}$ and $65\% \pm 2\%$ relative humidity for more than 48 h before measuring. The physical and mechanical strengths of the samples, including tensile strength, tearing strength, and elongation at break, were tested by a universal testing machine (GOTECH, China) according to ISO 3377-2: 2016 and ISO 3376: 2020.¹¹⁻¹²

Determination of free formaldehyde content in leather

The free formaldehyde contents of retanned leather samples were determined by HPLC method according to ISO/TS 17226: 2018.¹³

Results and discussion

Characterization of retanning agents

FTIR analysis

The FTIR spectra of TRP, CCI, and MUF are illustrated in Figure 3a, respectively.

The strong and wide peak at 3342 cm^{-1} in the spectra of the TRPs was assigned to the stretching vibrations of hydroxyl and second amino groups, indicating the successful conjugation of hydroxymethyl groups and melamine.¹⁴ A Mannich-type reaction occurred among diethanolamine, formaldehyde, and melamine. Due to the imino group of diethanolamine having a greater basicity than that of melamine's primary amino group, *N*-hydroxymethyl diethanolamine was first synthesized, and melamine was then combined to prepare TRP. Moreover, peaks at 1559 and 814 cm^{-1} were attributed to the vibration of triazine rings; the observation of these peaks in TRP is also a strong evidence of the successful reaction of melamine and formaldehyde.¹⁵ The peak at 2945 cm^{-1} is assigned to the stretching vibration of C-H bonds from diethanolamine, which further confirms the successful reaction.¹⁶ In the CCI spectra, the introduction of ECH can be proven by the

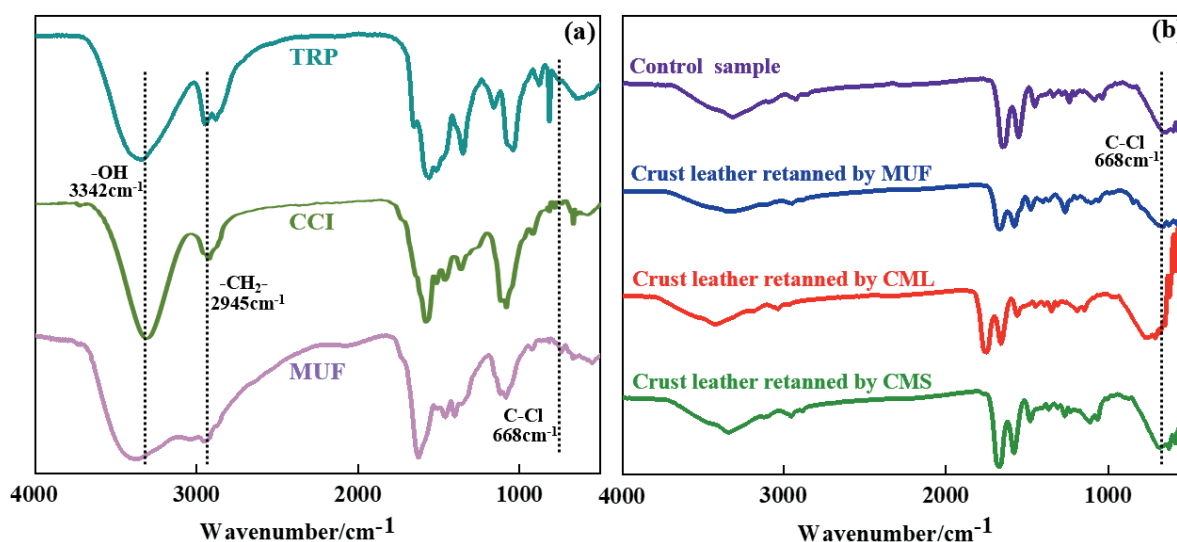


Figure 3. FTIR spectra of TRP, CCI, and MUF (a); FTIR spectra of crust leather retanned by MUF, CMS, CML and control sample (b).

C–Cl stretching vibration peak at 668 cm^{-1} .¹⁷ Moreover, the weak peak at 1083 cm^{-1} was attributed to ether bonds originating from the ring-opening reactions of epoxy groups, which also suggests the successful synthesis of CCI.¹⁸ After the introduction of lysine, the peak at 668 cm^{-1} , which was assigned to C–Cl stretching vibration, almost disappeared in the MUF spectra, indicating the occurrence of the nucleophilic substitution between the C–Cl of CCI and the $-\text{NH}_2$ of lysine. Moreover, the asymmetric and symmetric stretching vibrations of methylene from lysine can be observed at 2924 and 2853 cm^{-1} , respectively; the appearance of these peaks further proved the successful introduction of lysine.¹⁹

The FTIR spectra of the crust leather retanned by MUF, CMS, CML, and control sample are shown in Figure 3b. The absences of the C-Cl signal at 668 cm^{-1} in the spectra of all samples prove that there is no chloride contained in the crust leather.

NMR

^{13}C -NMR was further employed to confirm the structure of products, the results and the carbon atoms of TRP, CCI, and MUF are presented in Figures 4a–c. First, in the spectrum of TRP, signals of melamine triazine carbons can be observed at 167.47 , 167.11 , and 163.34 ppm , these three peaks are assigned to di-, tri-, and

monosubstituted melamine, respectively.²⁰ The appearance of these peaks indicates the successful reaction among diethanolamine, formaldehyde, and melamine. Moreover, the peaks at 60.62 and 56.02 ppm are attributed to the two $-\text{CH}_2-$ in diethanolamine, which further confirm the success of the reaction.²¹ Moreover, the peaks observed in the 58 – 60 ppm region are assigned to different hydroxymethyl groups, which suggests that few hydroxymethyl groups remained in TRP.²² Interestingly, the peak at 86.58 ppm is due to formaldehyde hydration.²³ Considering that a large excess of $-\text{NH}_2$ and $-\text{NH}-$ groups were formed in the synthesis process of TRP, the presence of this peak implies that the reaction between $-\text{CHO}$ and $-\text{NH}_2$ groups is incomplete and will finally maintain a delicate balance. For this reason, formaldehyde is hard to consume completely during synthesis; this reason also explains why the formaldehyde content stayed at a very high level in the synthesized MR compared with that obtained in the traditional methylation-condensation process.

In the ^{13}C -NMR spectrum of CCI, the peaks of different hydroxymethyl groups at the 58 – 60 ppm region disappeared, and only a single peak at 163.44 ppm was found. These changes were all related to the ring-opening reaction between $-\text{OH}/-\text{NH}_2$ and epoxy groups, indicating the successful introduction of $-\text{Cl}$.²⁴ Moreover,

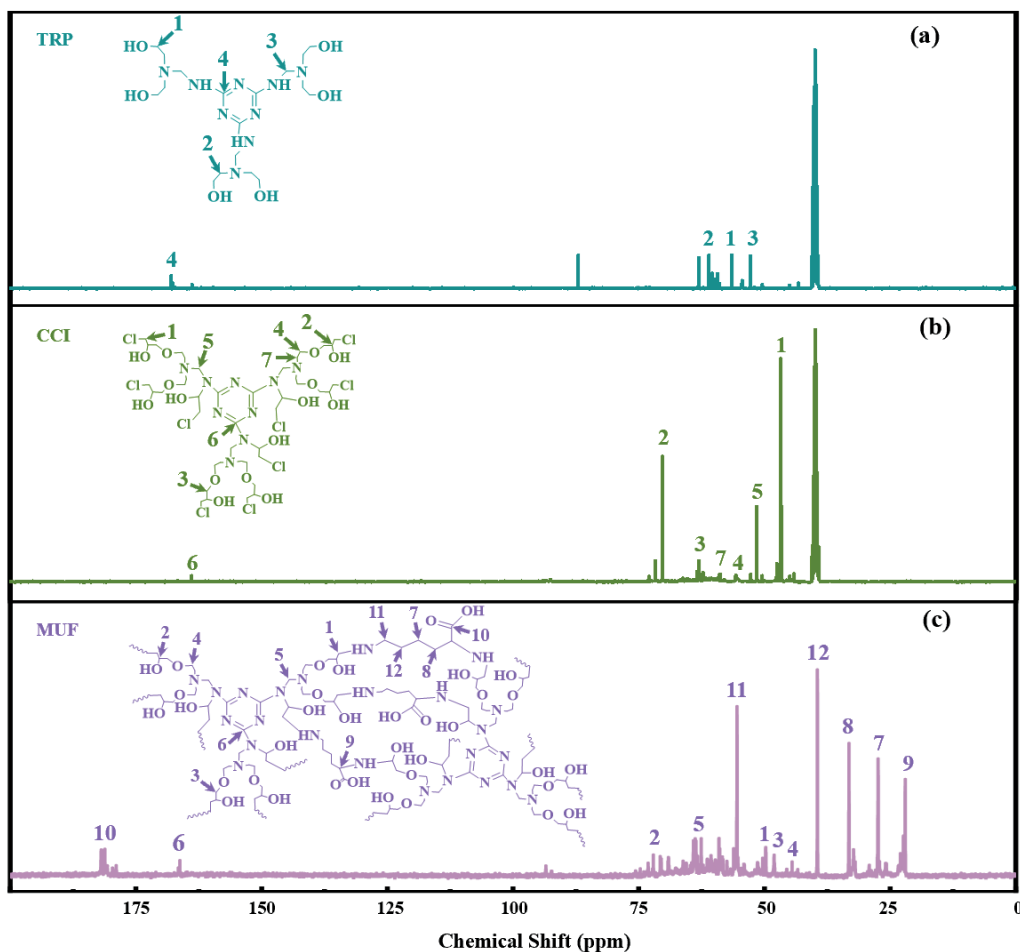


Figure 4. ^{13}C -NMR spectra of TRP (a), CCI (b), and MUF (c).

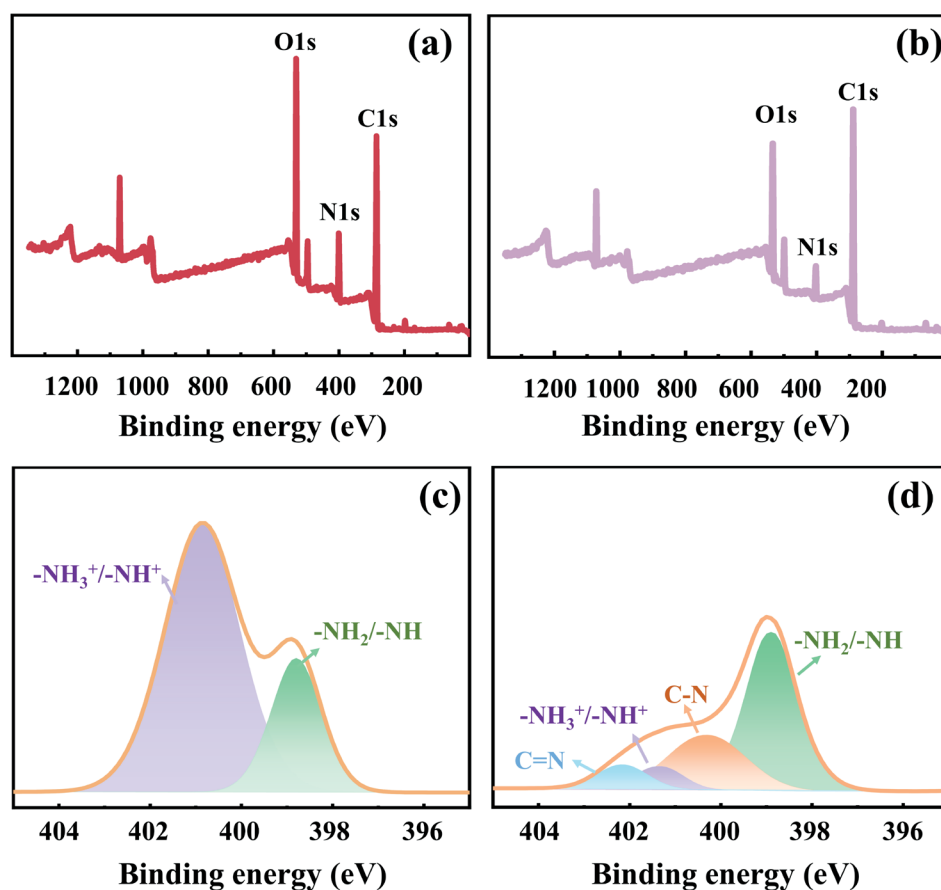


Figure 5. Survey scans of lysine (a) and MUF (b); N 1s XPS spectra of lysine (c) and MUF (d).

the newly appeared peaks at 46–48 ppm region in the spectra of CCI were assigned to the different types of carbon atoms that are linked to chlorine atoms. The appearances of these peaks prove the successful synthesis of CCI.²⁵

The final product of MUF was obtained after the polymerization of CCI was initiated by lysine. Figure 4c shows five strong peaks at 55.44, 39.47, 33.18, 27.39, and 22.01 ppm. These peaks are attributed to the methine and methylene carbons in lysine, indicating the nucleophilic substitution reaction between -NH_2 in lysine and -Cl in CCI.²⁶ Moreover, this reaction can also be evidenced by the disappearance of peaks at 46–48 ppm, which is assigned to carbon atoms linked to chlorine atoms. In addition, many small peaks are distributed at 47–52 and 57–77 ppm. These peaks correspond to different kinds of methyl in MUF. The occurrence of these peaks is attributed to the different degrees of substitution.²⁷

XPS analysis

The elemental and bond energy variations of lysine and MUF were further analyzed by XPS as shown in Figure 5. In the full XPS spectra of lysine and MUF, the absorption peaks with binding energies at 285, 400, and 531.2 eV are attributed to C 1s, N 1s, and O 1s, respectively, which are the major elemental compositions of lysine and MUF. The N spectrum of lysine in Figure 5c has two main peaks at 398.85 and 400.87 eV, corresponding to -NH_2 in the lysine molecule and ionic states -NH_3^+ and -NH^+ formed between the lysine molecules, respectively.²⁸ After reaction with CCI, the N spectrum of MUF (Figure 5d) shows four peaks at 399.06, 400.29, 401.31, and 402.16 eV, which are attributed to $\text{-NH}_2/\text{-NH}$, C-N, $\text{-NH}_3^+/\text{-NH}^+$, and C=N in MUF, respectively. Moreover, compared to Figure 5c, Figure 5d shows an obvious decrease in the intensity of $\text{NH}_3^+/\text{NH}^+$, further indicating that chlorine from CCI has successfully reacted with the deprotonated form of lysine.^{29–30}

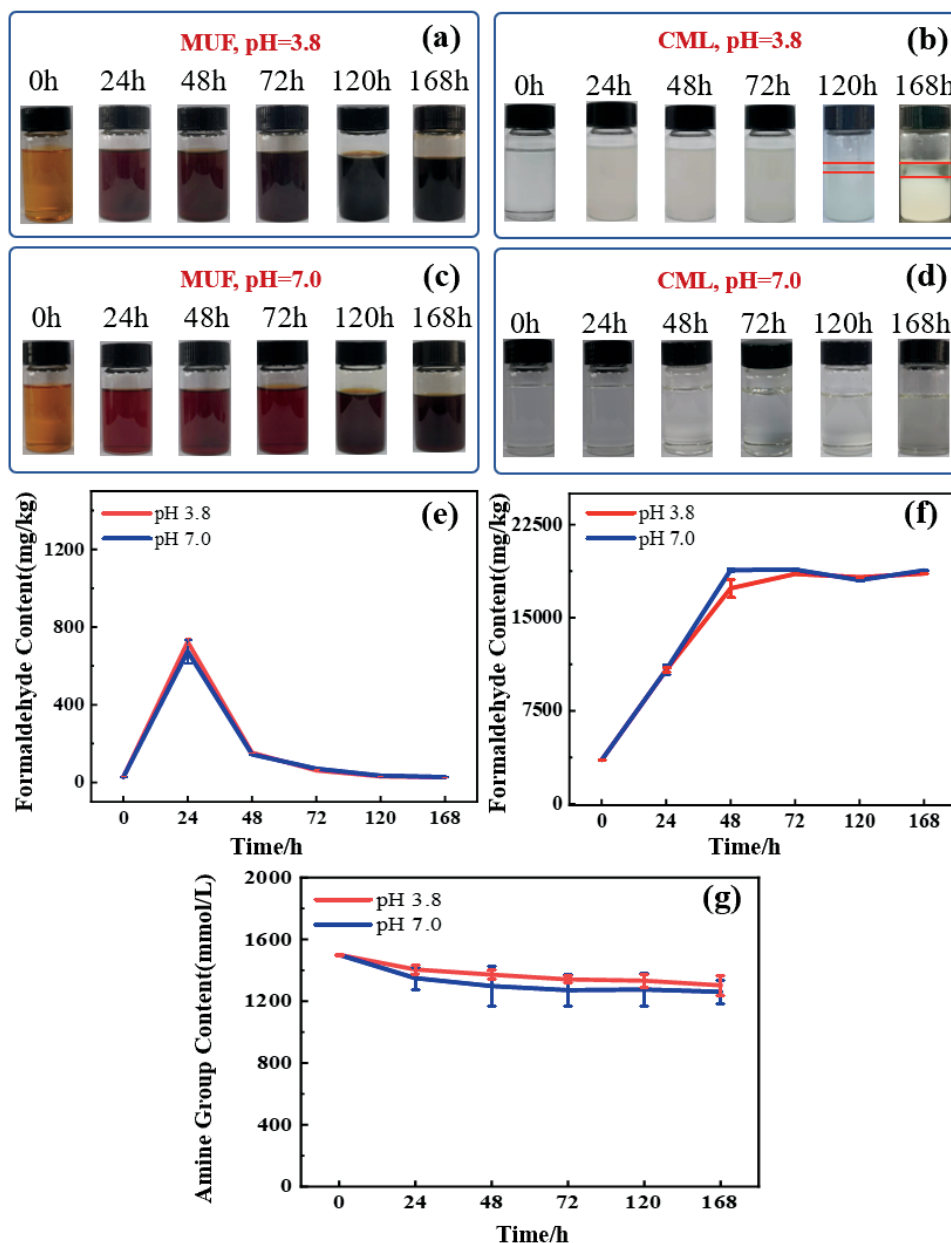


Figure 6. Stability of MUF at pH 3.8 (a), CML at pH 3.8 (b), MUF at pH 7.0 (c), and CML at pH 7.0 (d); formaldehyde content evolutions of MUF (e) and CML (f) during observation; amine group content evolutions of MUF (g) during observation.

Storage stability and formaldehyde determination of retanning agents

The storage stability of liquid MUF and CML at pH 3.8 and 7.0 were exhibited in Figures 6a–d. The alkaline conditions were not evaluated because the leather manufacturing processes were mostly conducted in acidic conditions. Storage stability is an important indicator of hydroxymethyl contents. Hydroxymethyl groups have high activity; they can condense with each other during storage and finally precipitate out.³¹ Precipitation was observed in CML at pH 3.8 after being placed at 80°C for 120 h, whereas MUF was stable during observations. CML was synthesized by the traditional

hydroxymethylation–condensation process, and large amounts of residual hydroxymethyl groups were found in the product. The residual hydroxymethyl groups will be further condensed and lead to an unstable state. However, hydroxymethyl groups were mostly consumed in MUF and thus show high stability even at an extremely low pH. Considering its very low content of hydroxymethyl groups, MUF should have ultralow-formaldehyde emission.

It can be observed in Figures 6a and 6c that the color of MUF became darker during storage testing. MUF is rich in hydroxyl groups, and some of them were oxidized to aldehydes and ketones

during storage at 80°C. These aldehydes and ketones interacted with free amino groups to cause the Maillard reaction, and finally resulted in an increase of the color intensity.³² Therefore, MUF is advised against storing in high-temperature environments.

The continuous release of free formaldehyde in MR is greatly related with the amount of methylene ether bonds. Figures 6e–f shows the formaldehyde content evolutions of CML and MUF during observation. The formaldehyde content of CML showed an increasing trend with time at different pH and tended to be stable after 72 h. This phenomenon can be attributed to the breakage of methylene ether bonds in CML, which can lead to the release of free formaldehyde. Afterward, the methylene ether bonds in CML were mostly consumed, and its formaldehyde content tended to stabilize. After 168 h, the formaldehyde content of CML were 18555.99 and 18813.90 mg/kg at pH 3.8 and 7.0, respectively. The formaldehyde content of MUF initially increased and then decreased. In the first step of MUF preparation, a small amount of methylene ether bonds were generated as shown in the ¹³C NMR analysis, which will breakdown, and release formaldehyde at a higher temperature. However, the maximum formaldehyde content of MUF was only 724.02 mg/kg, which was much lower than that of CML. The decreasing stage can be attributed to the presence of large amounts of $-NH_2/-NH$ in MUF. These groups can react with the released formaldehyde. After 168 h, the formaldehyde content in MUF greatly decreased to 26.14 and 28.23 mg/kg at pH 3.8 and 7.0, respectively, indicating the great advantage of the proposed new synthesis method for MUF. The amine group content changes of MUF over the course of storage were presented in Figure 6g. Before 72 hours, the amine group content was significantly decreased at pH 3.8 and 7.0, but it was almost unchanged after 72 hours, providing strong support for the reaction between $-NH_2/-NH$ and the released formaldehyde.

Particle size and zeta potential

The average particle sizes and zeta potentials of MUF, CML, and CMS are summarized in Figure 7. The average particle size of MUF was 392 nm, which was slightly lower than those of CMS (593 nm) and CML (587 nm). The particle size and size distribution of retanning agents greatly affect their retanning performance.³³ A particle size that is too large may result in insufficient leather penetration, whereas a small particle size may decrease the filling performance. According to literature, the diameter of collagen fibers in leather is approximately 0.5–20 μm , and the average spacing between fibers is 2.5 μm .³⁴ Therefore, MUF can easily penetrate leather and fill collagen fibers well.

Apart from particle size, the charges of retanning agents will also affect their penetration and uptake in leather. Chrome-tanned leather is positively charged, and retanning agents are usually designed as an anionic type to facilitate their absorption.³⁵ In chromium-free tanned leather, the charge mismatch between wet white and retanning agents will result in the poor quality of the finished leather. Fortunately, amphoteric agents are promising in solving the charge mismatch problem owing to their pH-responsive function.³⁶ As illustrated in Figure 7b, the pI values of MUF and CMS were 5.08 and 4.56, respectively. Lysine is a basic amino acid with two amino groups, which could increase the pI of MUF and is beneficial for the absorption of anionic retanning agents. However, CML is in the anionic state at pH 1–10 because of its high sulfonation degree.

Retanning performances of MUF

Absorption rates of retanning and fatliquoring agents

The absorption rates of retanning and fatliquoring agents were determined by collecting the bath at the beginning and end of the retanning and fatliquoring processes. The results are shown in

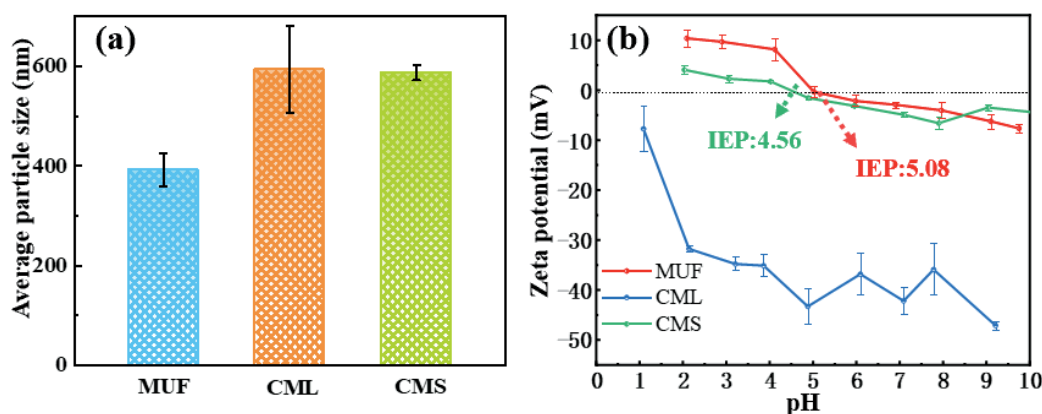


Figure 7. Average particle sizes (a) and zeta potentials (b) of MUF, CML, and CMS.

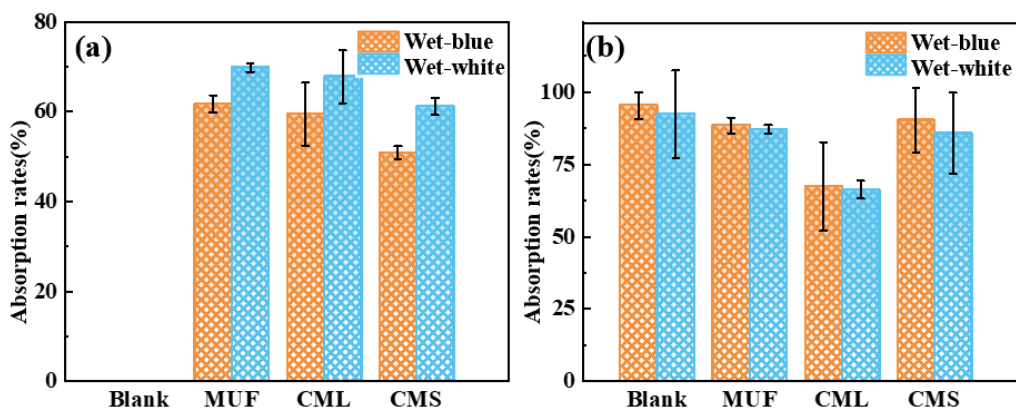


Figure 8. Absorption rates of retanning (a) and fatliquoring agents (b).

Figure 8. MUF exhibited a higher absorption rate than CML and CMS (Figure 8a). The absorption rate of CMS was the lowest in the chrome-tanned and chrome-free leather because of the poor solubility of CMS. Notably, compared with commercial MRs, the leather samples retanned by MUF manifested a high absorption rate by the fatliquoring agents in wet-blue and wet-white leathers (Figure 8b). The pH of the retanning process was about 5.5. MUF was in an anionic state in this condition, and the electrostatic attraction between MUF and collagen fiber is beneficial for its combination.³⁷ Moreover, in the following fatliquoring stage, the final pH of the bath was controlled at 3.8, at which MUF was in a cationic state and can further promote the absorption of anionic fatliquoring agents. This

result further proved the superiority of amphoteric retanning agents in leather manufacturing.

Physical and mechanical strengths

The physical and mechanical strengths of the leather samples retanned by MUF, CMS, and CML, including thickening rate, tensile strength, tear strength, and elongation at break, were thoroughly determined. As shown in Figure 9, the thickening rates of the wet-blue and wet-white leathers retanned by MUF were higher than those retanned by CMS but were lower than those retanned by CML (Figure 9a). The tensile strengths, tear strengths, and elongation at break of the leather samples retanned

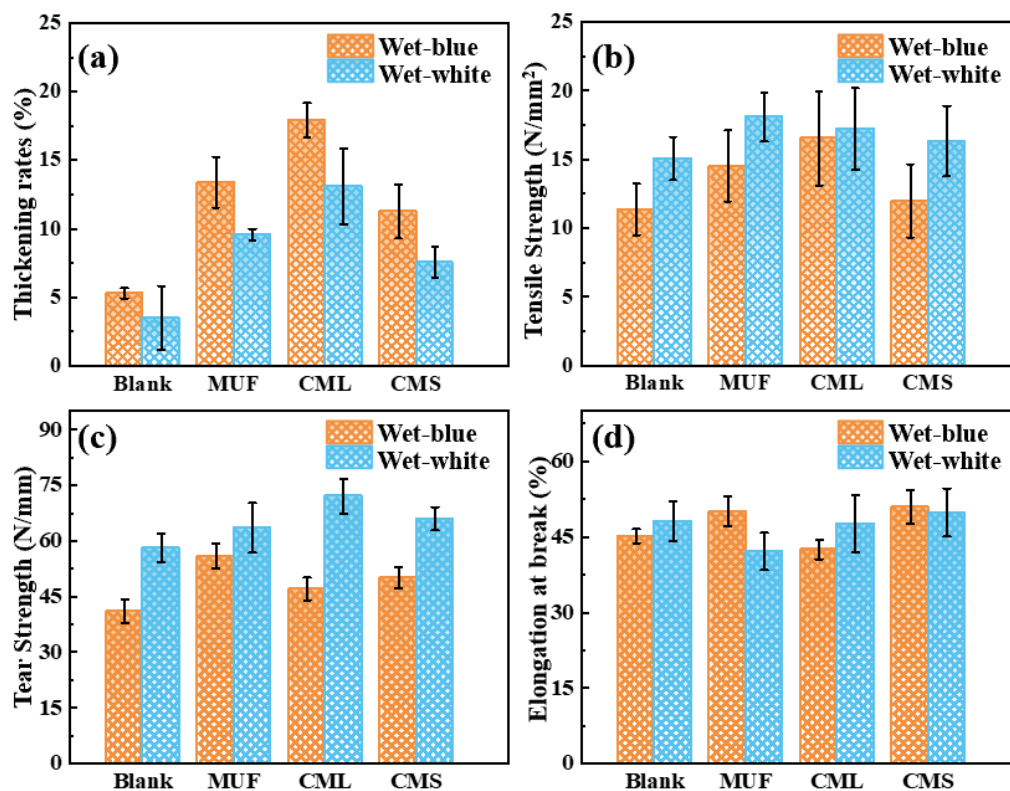


Figure 9. Physical and mechanical strengths of leather samples retanned by MUF, CML, and CMS: thickening rates (a), tensile strength (b), tear strength (c), and elongation at break (d).

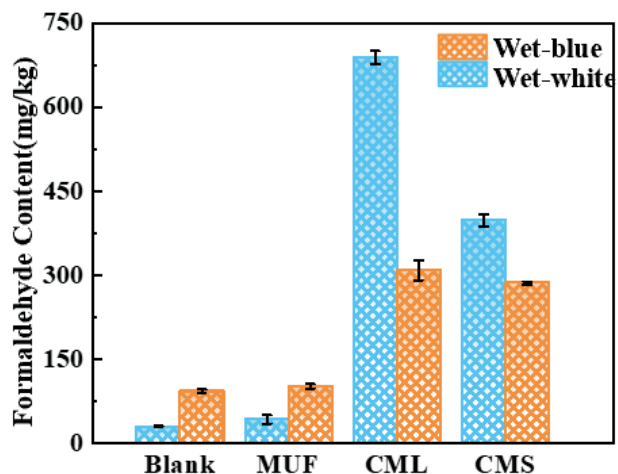


Figure 10. Formaldehyde contents of leather samples retanned by MUF, CML, and CMS.

by MUF were comparable to those retanned by CML and CMS; overall, MUF and CML showed better performances than CMS (Figures 9b–d). Compared with the blank, the tensile and tear strengths of the leathers retanned by MR were all enhanced (Figures 9b–c). In general, the retanning process often refers to the generation of cross-linked bonds between the retanning agents and collagen polypeptide chains. These bonds can improve the physical and mechanical strengths of the leather. In the molecular structures of MUF, $-OH$, $-NH_2$, and $-COOH$ groups may form multipoint cross-linking with collagen fibers and finally lead to the improvement of mechanical strength.

Determination of free formaldehyde in leather

Figure 10 shows the formaldehyde content of the leather samples retanned by different agents. The formaldehyde content in blank blue and white leather samples without retanning were 29.27 and 92.49 mg/kg, respectively, which possibly originated from the pretreatment and tanning process. After the samples were retanned by commercial MR retanning agents (CML and CMS), the formaldehyde content of wet-white and wet-blue leathers reached as high as 688.17/308.74 and 398.05/286.12 mg/kg, respectively. Compared with the blank samples, the formaldehyde contents of the wet-white and wet-blue leather samples retanned by MUF only increased by 12.68 and 8.98 mg/kg, respectively. These facts suggest that MUF application did not remarkably increase the formaldehyde content of leather. Economic analysis was conducted and the cost of UF was estimated within \$1.00/kg, which is comparable with commercial retanning agents, showing a promising application potential.

Conclusion

A new synthesis method was proposed in this study to solve the formaldehyde issue in MR, and an ultralow-formaldehyde MR retanning agent, MUF, was prepared. In the synthesis process, the introduction of diethanolamine changed the route of hydroxymethyl reaction and greatly reduced the residue of formaldehyde, and ECH changed the state of the intermediate product compared with the traditional approach. Importantly, the polymerization initiated by lysine extremely reduced the formation of methylene ether bonds, which fundamentally solved the continuous release of formaldehyde during storage and application. MUF could be applied in the retanning process of chrome-tanned leather and TWLZ (chrome-free)-tanned leather and exhibited outstanding retanning performances. Therefore, this novel MR preparation strategy is successful, and the obtained product has a good potential application prospect.

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Reference

- Yu, Y., Wang, H., Wang, Y. N., Zhou, J. F., Shi, B.; Construction of a chrome-free tanning system based on highly-oxidized starch-zirconium complexes. *JALCA*, **117**, 87–95, 2022.
- Kolisnyk, A., Chugai, A., Chernyakova, O., Kuzmina, V.; Methodical bases for taking into account the impact of air pollution on the population lifespan (on the example of the city of Odessa, Ukraine). *Ecol. Eng. Environ. Technol.* **23**, 40–46, 2022.
- Kristak, L., Antov, P., Bekhta, P., Lubis, M. A., Iswanto, A. H., Reh, R., Sedliacik, J., Savov, V., Taghiyari, H. R., Papadopoulos, A. N.; Recent progress in ultra-low formaldehyde emitting adhesive systems and formaldehyde scavengers in wood-based panels: a review. *Wood Mater. Sci. Eng.* **17**, 1–20, 2022.
- Peng, L. Q., Long, W. J., Zhang, W. H., Shi, B.; Leaching toxicity and ecotoxicity of tanned leather waste during production phase. *Process Saf. Environ. Prot.* **161**, 201–209, 2022.
- Yang, M. L., Rosentrater, K. A.; Life cycle assessment of urea-formaldehyde adhesive and phenol-formaldehyde adhesives. *Environ. Processes*, **7**, 553–561, 2020.
- Wang, Y. S., Sun, X. L., Han, Q. X., James, T. D., Wang, X. C.; Highly sensitive and selective water-soluble fluorescent probe for the detection of formaldehyde in leather products. *Dyes Pigm.* **188**, 109175, 2021.
- Dorieh, A., Pour, M. F., Movahed, S. G., Pizza, A., Selakjani, P. P., Kiamahalleh, M. V., Hatefnia, H., Shahavi, M. H., Aghaei, R.; A review of recent progress in melamine-formaldehyde resin based nanocomposites as coating materials. *Prog. Org. Coat.* **165**, 106768, 2022.
- Seidl, R., Weiss, S., Zikulnig-Rusch, E. M., Kandelbauer, A.; Response surface optimization for improving the processing behavior of melamine formaldehyde impregnation resins. *J. Appl. Polym. Sci.* **138**, 50181, 2021.
- Yi, Y. D., Ding, W., Wang, Y. N., Shi, B.; Determination of free formaldehyde in leather chemicals. *JALCA*, **114**, 382–390, 2019.
- Sabeti Meybod, J., Ostad Movahed, S.; The effects of several parameters on the storage stability of the melamine-formaldehyde (MF) polymers by using a traditional design of experiment (DOE) software. *J. Adhes. Sci. Technol.* **34**, 1705–1719, 2020.
- IUP 6.; Measurement of tensile strength and percentage elongation. *JSLTC*, **84**, 317–321, 2000.
- IUP 8.; Measurement of tear load—double edge tear. *JSLTC*, **84**, 327–329, 2000.
- ISO 17226-1:2018 Leather - chemical determination of formaldehyde content - part 1: method using high performance liquid chromatography (second edition).
- Zhou, J. B., Zhou, J. F., Li, P. L., Liao, X. P., Shi, B.; Preparation of formaldehyde-free melamine resin using furfural as condensation agent and its retanning performances investigation. *JALCA*, **113**, 198–206, 2018.
- Huang, Y. L., Li, W., Xu, Y. W., Ding, M., Ding, J., Zhang, Y., Wang, Y. H., Chen, S. Y., Jin, Y. D., Xia, C. Q.; Rapid iodine adsorption from vapor phase and solution by a nitrogen-rich covalent piperazine-triazine-based polymer. *New J. Chem.* **45**, 5363–5370, 2021.
- Zhang, X. P., Duan, Z. K., Zhao, Y. L., Wu, Y. Y., Qiu, T., Shi, X. L.; Direct determination of diethanolamine in high salinity dehydrogenation reaction solutions by ion chromatography (IC). *Anal. Lett.* **55**, 57–67, 2022.
- Satheeshkumar, C., Jung, B. J., Jang, H., Lee, W., Seo, M.; Surface modification of parylene C film via buchwald-hartwig amination for organic solvent-compatible and flexible microfluidic channel bonding. *Macromol. Rapid Commun.* **42**, 2000520, 2021.
- Demiral, İ., Samdan, C., Demiral, H.; Enrichment of the surface functional groups of activated carbon by modification method. *Surf. Interfaces*, **22**, 100873, 2021.
- Yang, X., Wang, B. L., Sha, D., Liu, Y. G., Xu, J. D., Shi, K., Yu, C., Ji, X. L.; Injectable and antibacterial ϵ -poly (L-lysine)-modified poly (vinyl alcohol)/chitosan/AgNPs hydrogels as wound healing dressings. *Polymer*, **212**, 123155, 2021.
- He, F., Wang, M., Luo, L., Wang, Z. X., Peng, S. Q., Li, Y. X.; Directional modulation of triazine and heptazine based carbon nitride for efficient photocatalytic H_2 evolution. *Appl. Surf. Sci.* **562**, 150103, 2021.
- García-Abuín, A., Gomez-Díaz, D., Lopez, A. B., Navaza, J. M., Rumbo, A.; NMR characterization of carbon dioxide chemical absorption with monoethanolamine, diethanolamine, and triethanolamine. *Ind. Eng. Chem. Res.* **52**, 13432–13438, 2013.
- Ruda, A., Widmalm, G., Wohlert, J.; O-Methylation in Carbohydrates: An NMR and MD simulation study with application to methylcellulose. *J. Phys. Chem. B*, **125**, 11967–11979, 2021.
- Panangama, L., Pizzi, A.; A ^{13}C -NMR analysis method for MUF and MF resin strength and formaldehyde emission. *J. Appl. Polym. Sci.* **59**, 2055–2068, 1996.
- Tohmura, S. I., Inoue, A., Sahari, S. A.; Influence of the melamine content in melamine-urea-formaldehyde resins on formaldehyde emission and cured resin structure. *J. Wood Sci.* **47**, 451–457, 2001.
- Berger, S., Bock, W., Frenking, G., Jonas, G., Mueller, F.; NMR data of methyltitanium trichloride and related organometallic compounds. A combined experimental and theoretical study of Me_nXCl_{4-n} ($n = 0-4$; $X = C, Si, Sn, Pb, Ti$). *J. Am. Chem. Soc.* **117**, 3820–3829, 1995.
- Sheveleva, N. N., Markelov, D. A., Vovk, M. A., Mikhailova, M. E., Tarasenko, I. I., Tolstoy, P. M., Neelov, L. M., Lähderanta, E.; Lysine-based dendrimer with double arginine residues. *RSC Adv.* **9**, 18018–18026, 2019.
- Busico, V., Cipullo, R., Monaco, G., Vacatello, M., Segre, A. L.; Full assignment of the ^{13}C -NMR spectra of regioregular polypropylenes: methyl and methylene region. *Macromolecules*, **30**, 6251–6263, 1997.
- Liu, Z. H., Wang, Q. M., Lü, Q. F.; L-lysine functionalized $Ti_3C_2T_x$ coated polyurethane sponge for high-throughput oil–water separation. *Colloids Surf. A Physicochem. Eng. Asp.* **640**, 128396, 2022.

29. Lu, F. F., Dong, A. Q., Ding, G. J., Xu, K., Li, J. M., You, L. J.; Magnetic porous polymer composite for high performance adsorption of acid red 18 based on melamine resin and chitosan. *J. Mol. Liq.* **294**, 111515, 2019.
 30. Guo, X. J., Gao, G., Remón, J., Ma, Y., Jiang, Z. C., Shi, B., Tsang, D. C.; Selective hydrogenation of vanillin to vanillyl alcohol over Pd, Pt, and Au catalysts supported on an advanced nitrogen-containing carbon material produced from food waste. *Chem. Eng. J.* **440**, 135885, 2022.
 31. Gao, D. G., Wang, P. P., Shi, J. B., Li, F., Li, W. B., Lü, B., Ma, J. Z.; A green chemistry approach to leather tanning process: cage-like octa (aminosilsesquioxane) combined with tetrakis (hydroxymethyl) phosphonium sulfate. *J. Clean. Prod.* **229**, 1102–1111, 2019.
 32. Meng, X. Y., Li T. T., Song T, Chen, C., Venkitasamy, C., Pan, Z. L., Zhang, H. E.; Solubility, structural properties, and immunomodulatory activities of rice dreg protein modified with sodium alginate under microwave heating. *Food Sci. Nutr.* **7**, 2556-2564, 2019.
 33. Huang, W. L., Song, Y., Yu, Y., Wang, Y. N., Shi, B.; Interaction between retanning agents and wet white tanned by a novel bimetal complex tanning agent. *J. Leather Sci. Eng.* **2**, 8, 2020.
 34. Wang, X. C., Lan, X. M., Zhu, X., Sun, S. W.; Preparation of a ricinoleic acid modified amphoteric polyurethane for leather cleaner and simplifying production. *J. Clean. Prod.* **330**, 129877, 2022.
 35. Wang, X. C., Sun, S. W., Zhu, X., Guo, P. Y., Liu, X. H., Liu, C. L., Li, M.; Application of amphoteric polymers in the process of leather post-tanning. *J. Leather Sci. Eng.* **3**, 9, 2021.
 36. Li, Q. J., Yi, Y. D., Wang, Y. N., Li, J., Shi, B.; Effect of cationic monomer structure on the aggregation behavior of amphoteric acrylic polymer around isoelectric point. *J. Leather Sci. Eng.* **4**, 4, 2022.
 37. Yu, Y., Sun, Q. Y., Zeng, Y. H., Lin, Y. R., Wang, Y. N., Shi, B.; Diagnosing the environmental impacts of typical fatliquors in leather manufacture from life cycle assessment perspective. *J. Leather Sci. Eng.* **4**, 6, 2022.
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Removal of Anionic Dye from Tannery Wastewater Using Peanut Shell Waste as a Biosorbent

by

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Abstract

Contamination of water bodies by organic substances, such as dyes, cause impacts on the environment and human health. Furthermore, the search for environmentally appropriate destinations for solid waste, such as those from agro-industries, has been intensifying, to minimize the impact of the growing generation of waste as a result of population growth. Thus, this work aimed to evaluate the use of raw peanut shells as an alternative adsorbent for the removal of Brown acid dye from synthetic leather dyeing wastewater. The peanut shells were milled and sieved. The material was characterized by Fourier Transform Infrared Spectroscopy. The parameters evaluated in the adsorption tests were pH, contact time, and mass of adsorbent material. The maximum adsorption capacity verified for the peanut shell was 7.753 mg/g and up to 93% of the dye was removed. The best adsorption conditions were at pH 2.5, 10 minutes, and adsorbent mass of 0.3 g in 50 mL of effluent. The results showed relevant removal of the Brown acid dye by the peanut shells' adsorbent material.

Introduction

Leather processing consists of a sequence of physical-chemical and mechanical operations applied to the raw hide using water and organic and inorganic chemicals. During the post-tanning stage, specific characteristics are conferred for each leather application, such as color, mechanical strength, and softness. An average of 360.2 kg of chemicals are applied per ton of shaved leather in the post-tanning process.¹ Among the chemicals used are dyes, which are natural or synthetic complex organic molecules. Dyes are commercially named as direct, acidic, reactive, dispersed, and basic, among others. In the leather dyeing stage, the most used dyes are acidic and reactive. During the process, 20% of the dye load does not fix to the leather and is discharged along with the wastewater. About 700 thousand tons/year of dyes are manufactured in the world, with acid dyes being the second-largest commercialized class, finding wide application in leather process.^{2,3} Dyes make the wastewater treatment difficult. The presence of dyes in formulations, such as azo and metal complexes, inhibits aquatic life growth,⁴ and induces acute and chronic cytotoxicity.^{4,5,6}

The treatment conventionally used for tannery wastewater consists of the application of equalization and neutralization operations, physical-chemical treatment through coagulation and flocculation followed by sedimentation, and biological treatment, with activated sludge being applied more frequently.⁷ However, the literature points to sludge generation and low efficiencies for the removal of salts and recalcitrant compounds (including dyes) as vulnerabilities of this treatment.⁷⁻¹⁴ Furthermore, environmental regulation is increasingly restrictive regarding the standards for releasing effluents into water bodies, and conventional treatment does not meet the requirements for the reuse of treated effluents in the process.⁷

To overcome the vulnerabilities of conventional treatment of tannery wastewater, advanced technologies have been studied. Adsorption is among the technologies adopted due to its low initial investment and operating costs, simplicity of operation, and high efficiency compared to conventional processes.^{2,3,15} Alternative adsorbents such as bark, seeds, and bagasse wastes have already shown high efficiency in the removal of dyes from industrial effluents, presenting low cost, easy obtaining, high volume generated, and simple preparation of the adsorbent.¹⁶ However, the use of peanut shells as a biosorbent for the removal of dyes from the leather industry still needs to be investigated. Thus, this work aimed to evaluate the use of peanut shells as an alternative adsorbent for the treatment of tannery wastewater, applied to the removal of Brown acid dye. The use of an adsorbent prepared with minimal application of chemicals, energy, and water was also an objective of this study, applying only peanut shell size reduction and sieving for the preparation of the sorbent material.

Experimental

Preparation of peanut shells

The raw peanut shells (Figure 1a) were selected, removing impurities. They were milled in a blender and classified in an electromagnetic sieve shaker for 30 minutes, obtaining a fraction of solids passing through the Tyler 42 mesh sieve (0.351 mm) (Figure 1b). After preparation, the peanut shells were stored in a desiccator.

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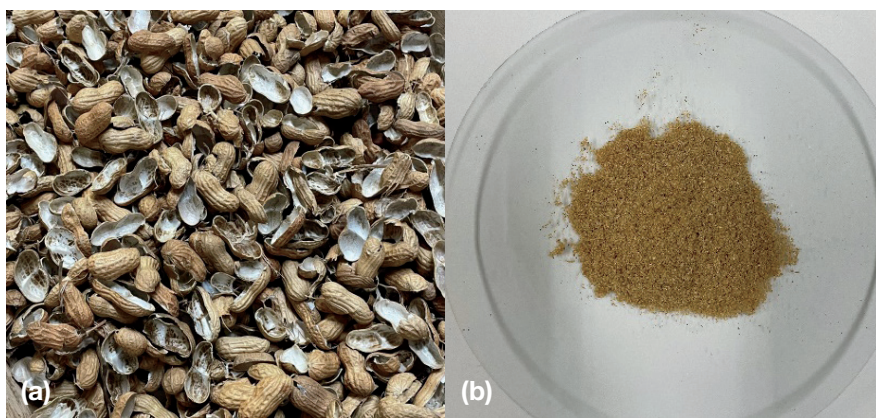


Figure 1. Peanut shells before (a) and after (b) the milling and sieving process

Analysis of peanut shells by Fourier Transform Infrared Spectroscopy

Peanut shells prepared by milling and sieving were characterized by Fourier Transform Infrared Spectroscopy (FTIR) before and after adsorption tests. FTIR analyzes were performed in the region of 4,000-650 cm^{-1} , with a resolution of 4 cm^{-1} in the Agilent Cary 630 equipment. The analysis aimed to evaluate the main functional groups present in the peanut shell that allow its binding with the Brown acid dye.

Preparation of synthetic wastewater containing dye

The Brown acid dye (CAS number 70210-34-3) was used in this work. The chemical structure of the dye (Figure 2) presents sulfone and nitro functional groups that are negatively charged sites capable of binding to the leather structure. In this study, the synthetic effluent consisted of a Brown acid dye solution at a concentration of 50 mg/L. A UV-Visible spectrophotometer (SP-220 Biospectro) was used to determine the dye concentration. Measurements were determined at the wavelength of maximum absorbance (468 nm).

Adsorption experiments

The variables evaluated in the adsorption experiments were pH, time, and adsorbent mass. The efficiency of dye removal from synthetic wastewater was determined using equation 1 and the amount of dye adsorbed per gram of adsorbent was calculated using equation 2. All analyzes were performed in duplicate.

$$\% \text{ Removal} = \frac{C_o - C_f}{C_o} \times 100 \quad (1)$$

$$q_t = \frac{(C_o - C_f) * V}{m_{ads}} \quad (2)$$

Where:

C_o – initial concentration of Brown acid dye (mg/L)

C_f – final concentration of Brown acid dye (mg/L)

q_t – amount of dye adsorbed (mg/g)

V – volume of solution (L)

m_{ads} – mass of adsorbent (g)

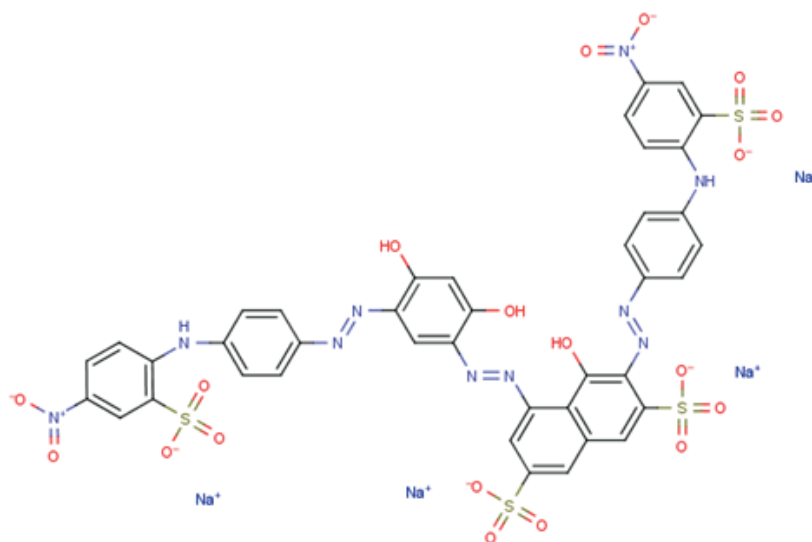


Figure 2. Chemical structure of the Brown acid dye

To determine the best pH for adsorption of the Brown acid dye, 50 mL of synthetic wastewater (50 mg/L of Brown acid dye) were added to 250 mL Erlenmeyer and 0.5 g of peanut shells were used. The pH was adjusted to 2.50, 4.00, 5.00, 6.00, 7.00, 8.00 and 9.00, with 0.1 mol/L HCl and 0.1 mol/L NaOH solutions. The system was stirred at 100 rpm at 25°C for 24 hours to ensure equilibrium between the solid and liquid phases. After this process, the solutions were centrifuged at 10,000 rpm for 10 minutes and the absorbance was measured using a UV-visible spectrophotometer with a wavelength of 468 nm.

The pH that showed the highest efficiency in the removal of the Brown acid dye was used to evaluate the influence of the adsorption time on wastewater treatment. Fifty milliliters of synthetic wastewater (50 mg/L of Brown acid dye) and 0.5 g of peanut shell were added to 250 mL Erlenmeyer. The Erlenmeyer was stirred at 100 rpm at 25°C. The removal efficiency (equation 1) of the Brown acid dye was evaluated at time intervals of 10, 30, 60, 90, 120, 150, and 180 minutes. The solutions were centrifuged at 10,000 rpm for 10 minutes and the absorbance was measured using a UV-visible spectrophotometer at a wavelength of 468 nm.

The experiments to evaluate the effect of the adsorbent mass on dye removal were carried out in 250 mL Erlenmeyers containing 0.3, 0.4, 0.5, 0.6, and 0.7 g of the adsorbent material and 50 mL synthetic wastewater (50 mg/L Brown acid dye). The Erlenmeyers were stirred at 100 rpm for 90 minutes at 25°C. The solutions were centrifuged at 10,000 rpm for 10 minutes and the absorbance was measured in a UV-visible spectrophotometer with a wavelength of 468 nm.

Statistical analysis

Dye removal data obtained for different pH values, contact times, and adsorbent mass were analyzed by one-way Analysis of Variance (ANOVA) followed by Tukey's post-hoc test and were considered significant when $p < 0.05$. All statistical analyzes were performed using GraphPad Prism 5.0 software.

Results and discussion

Analysis of peanut shells by Fourier Transform Infrared Spectroscopy

The peanut shell FTIR spectra are shown in Figure 3, before (Figure 3a) and after (Figure 3b) adsorption of the Brown acid dye.

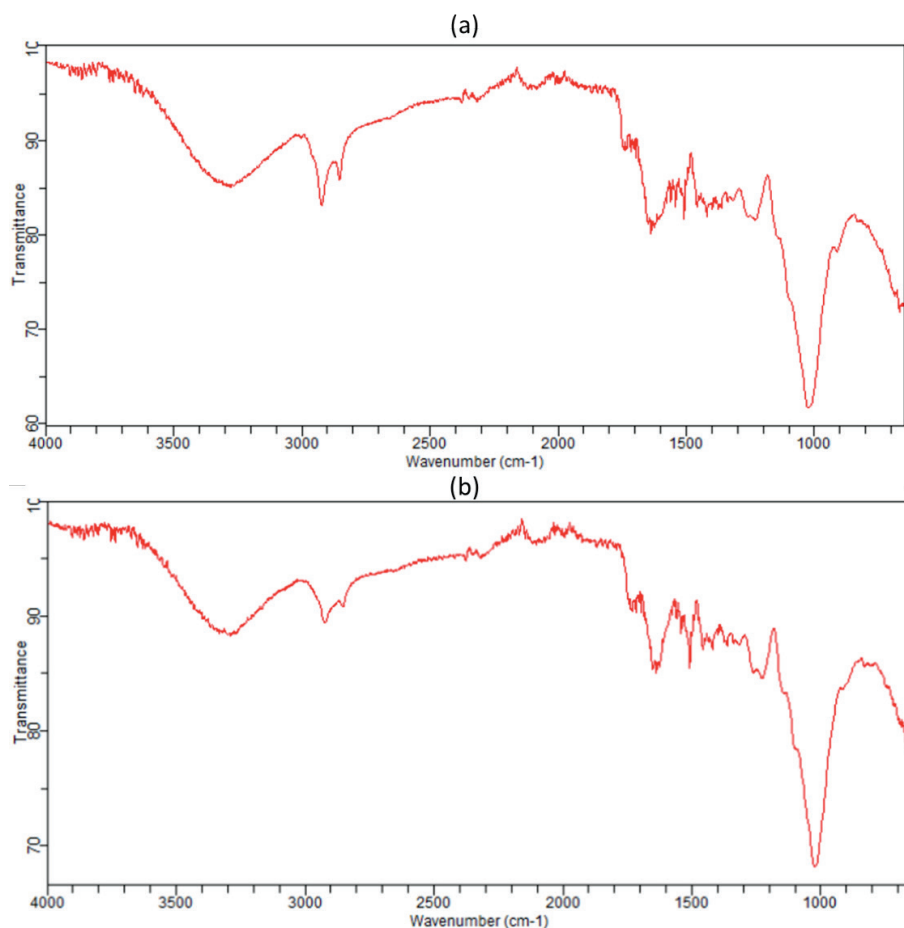


Figure 3. FTIR spectra of peanut shell before (a) and after (b) adsorption experiments

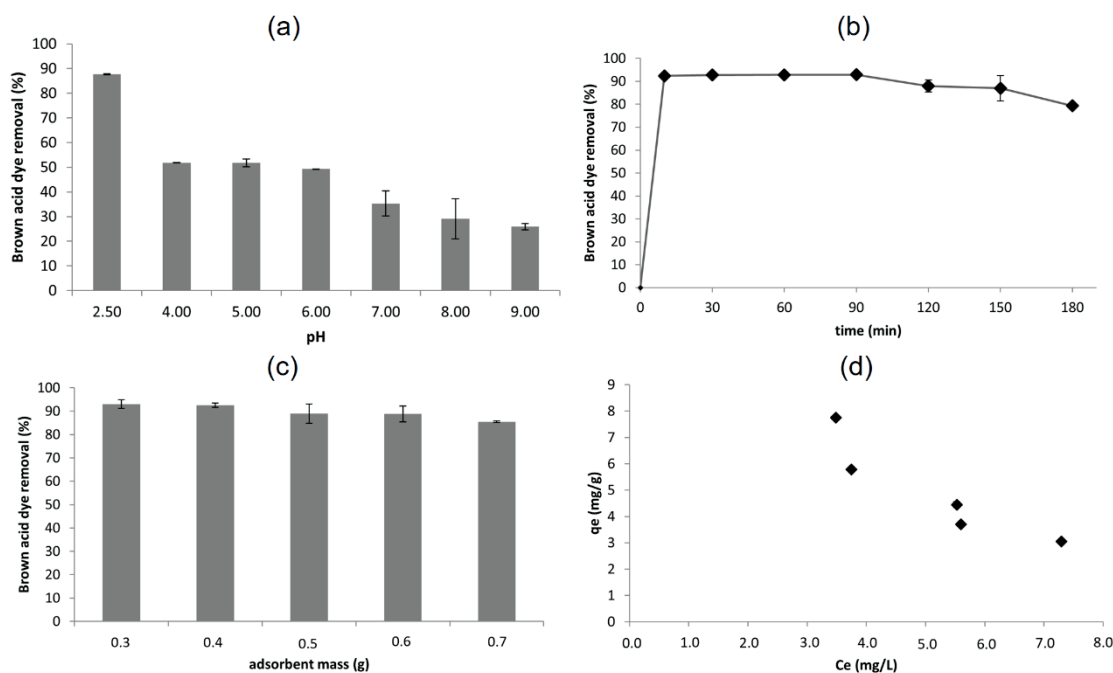


Figure 4. Effect of pH (a), time (b) and adsorbent mass (c) on Brown acid dye removal, and sorption capacity by peanut shells (d).

The FTIR spectra (Figure 3a) showed in the range from 3200 to 3500 cm^{-1} a band that belong to the functional groups -OH and/or -NH. Around 2800 and 3000 cm^{-1} , vibrational peaks with asymmetric and symmetrical stretching, respectively, of the C-H bond of CH_2 groups were verified (Figure 3a). The band around 1700 cm^{-1} is characteristic of the stretching of C=O, a possible constituent of carbonyl, carboxyl or aromatic compounds. The vibrations at 1400 and 1050 cm^{-1} can be attributed to the C-O bonds of the carboxylic and alcoholic groups. A band between 1300 and 1400 cm^{-1} represents the methyl group CH_3 and between 1350 and 1550 cm^{-1} the nitro group¹⁷. The groups amide, carboxyl, and hydroxyl in the chemical composition of the biomass structure is related to the presence of proteins, fatty acids and carbohydrates in the peanut shell.^{18,19} Also, the CH_2 groups can represent the lipidic compounds in the peanut shell. The C=O functional group is also present in the chemical structure of lipids.²⁰

The chemical structure of the Brown acid dye (Figure 2) presents sulfone and nitro groups, and the FTIR analysis showed that the raw peanut shell (Figure 3a) contains amide groups. Thus, considering that the acidic environment can protonate the amide groups²¹ present in the structure of the peanut shell, it is possible to observe the potential interaction of the sulfone and nitro groups (negatively charged) present in the dye with the amide groups (positively charged) in the peanut shell, enabling the adsorption process.

The superposition of the FTIR spectra before (Figure 3a) and after (Figure 3b) the adsorption experiments showed changes in the region of 1700 cm^{-1} , with a modification in the peak of the C=O bond. Furthermore, in the region of 1500 and 1600 cm^{-1} , a vibration from the N-H bond occurred, possibly due to the interaction of the amide group in the peanut shell with the sulfone and nitro groups in the Brown acid dye.

Adsorption experiments

The results of Brown acid dye removal are shown in Figure 4 under different conditions of pH (Figure 4a), adsorption time (Figure 4b), adsorbent mass (Figure 4c). The sorption capacity of Brown acid dye by peanut shells is also presented (Figure 4d).

The wastewater pH affects dye removal since the surface charge of the adsorbent controls the interaction of its ions. The Brown acid dye has sulfone and nitro anionic groups, thus, a positive charge on the surface of the biosorbent must have a higher and better dye adsorption ability.²² The maximum removal occurred at pH 2.5 (Figure 4a), where the amount of H^+ ions increases, improving the electrostatic attraction between the dye and the biosorbent.²³

The statistical analysis of the experimental data showed a significant difference among the various pH values used in the adsorption ($p < 0.0001$). Tukey's post-hoc test showed that there was a significant

difference in dye removal when pH 2.5 was compared with the other pH values, confirming that Brown acid dye removal is significantly higher at pH 2.5. There was no significant difference in dye removal when pH values 4.0, 5.0 and 6.0 were compared. This pH range shows intermediate efficiency for dye removal. When comparing the removal efficiency for pH values 7.0, 8.0 and 9.0, there was also no significant difference, with this pH range being the least efficient.

A previous study²⁴ found that the zero-charge point of peanut shells occurs at $\text{pH } 7.10 \pm 0.10$. Values of pH below the zero-charge point cause a positive charge to the peanut shell surface, and pH values above the zero-charge point cause a negative charge to the adsorbent surface.²⁵ This zero-charge point is consistent with the results found in this study for adsorption at different pH values, with higher removals at pH values below 7.0.

The evaluation of the adsorption time of the Brown acid dye was carried out in the best pH condition found in the previous step (pH 2.5). The dye removals for the tested contact times are presented in Figure 4b. High removals were promptly achieved. Removal efficiencies greater 92% were obtained in the first 10 minutes of adsorption. This behavior occurs due to the free sites on the surface of the adsorbent material, considering that at the beginning of the adsorption process, the binding sites are available in greater quantity.²⁶ Maximum removal occurred at 90 minutes ($92.9 \pm 0.1\%$). After this period the removal efficiency gradually decreased.

The statistical analysis of the data showed a significant difference in the dye removals obtained for the contact times ($p = 0.0051$). Tukey's post-hoc test showed that although the highest dye removal occurred at 90 minutes, no statistical difference was identified in removal efficiency for the period from 10 to 150 minutes. Though, the removal was significantly lower when the adsorption was carried out up to 180 minutes. The reduction of removal with time is not an expected behavior in an adsorption process and may be related to the release of colored compounds from the adsorbent material due to the similarity between the colors of the peanut shell and the Brown acid dye. When peanut shells were used to remove blue dyes from the textile industry (Reactive Blue 203²⁷ and methylene blue²⁴), and yellow, green, and amaranth anionic dyes,²⁸ this effect was not observed, supporting the theory that peanut shells released substances with a color similar to the Brown acid dye evaluated in the present study.

The effect of the adsorbent mass on the dye removal efficiency was evaluated under the best conditions of pH (2.5) and adsorption time (90 minutes). Dye removal efficiencies are presented in Figure 4c. The results demonstrate higher dye removal efficiencies for the 0.3 g ($93.0 \pm 1.9\%$) and 0.4 g ($92.5 \pm 0.9\%$) peanut shell masses. The removal ratio decreased when the adsorbent mass increased,

with removal efficiencies between $88.8 \pm 3.4\%$ and $85.4 \pm 0.3\%$ for the peanut shell masses of 0.6 and 0.7 grams, respectively. These results are consistent with the phenomenon observed in the time experiments. They corroborate the thesis that although the adsorbent material can remove the Brown acid dye, it releases colored substances with increasing time and adsorbent mass. The statistical analysis of the data indicated that, despite the behavior of the experimental data showing that the increase in the adsorbent mass reduces the dye removal, no significant differences were observed with the different adsorbent masses ($p=0.1376$).

The sorption capacity of Brown acid dye by peanut shells (q_e) (Figure 4d) was calculated (equation 2) and evaluated as a function of the dye concentration in the liquid phase. This evaluation demonstrates how the dye molecules are distributed between the biosorbent and the synthetic wastewater. The highest sorption capacity occurred with the lowest peanut shell masses. The dye concentrations in the synthetic wastewater after adsorption were $3.5 \pm 0.9 \text{ mg/L}$ and $3.7 \pm 0.5 \text{ mg/L}$ for the 0.3 and 0.4 g of peanut shell masses, respectively. Thus, the equilibrium concentrations (C_e) were the lowest for the lowest masses of adsorbent. When the mass of adsorbent increases, a decrease in color removal is observed. This behavior is not expected as the dye removal generally increases with the amount of adsorbent and the number of adsorption sites.²⁹ However, this behavior can be attributed to colored substances released by peanut shells used in the present study. The highest sorption capacity experimentally obtained was 7.753 mg/g. The maximum sorption capacities and removal efficiencies obtained by other studies that applied raw peanut shells are shown in Table I.

The maximum removal efficiency of the Brown acid dye obtained in the present study (93%) was superior to the removal of the Reactive blue 203²⁷ and the Crystal violet¹⁹ dyes, being close to the removal efficiencies of Amaranth, Sunset yellow, Fast green FCF²⁸ and Methylene blue.²⁴ Due to the sorption capacity decreasing with increasing adsorbent dosage, the sorption capacity obtained in the present study was lower than that obtained for other dyes, but above the sorption capacity found for the methylene blue dye.²⁴

The spent adsorbent applied to remove the Brown acid dye may require disposal after desorption of the dye or disposal even without desorption. There are four approaches that have been employed in the management, disposal and reuse of used adsorbents:³⁰ reuse (as soil amendment, depending on material toxicity), incineration (facilitating recovery of energy and hazardous materials), landfill (depending on the concentration of adsorbate in the spent adsorbent) and other safe disposals (e.g.: stabilization/solidification in inert material³¹ and phytoremediation). Additional research related to recovery, regeneration and final disposal of used adsorbents is needed to deliver better results and provide a new management path.³⁰

Table I
Removal efficiency and sorption capacity of dyes by peanut shell

Dye	Removal efficiency (%)	Sorption capacity (mg.g ⁻¹)	Author
Reactive Blue 203 (textile reactive dye)	66.83 %	49.29	27
Amaranth (Am), Sunset yellow (SY) and Fast green FCF (FG)	Am: 98.7 % SY: 99.57 % FG: 99.12%	Am: 14.90 SY: 13.99 FG: 15.60	28
Methylene blue (textile basic dye)	> 90 %	3.65	24
Crystal violet (cationic dye)	74 %	24.37	19

Conclusion

The results presented in this work showed the possible use of raw peanut shells as an adsorbent for the removal of Brown acid dye from wastewater. The adsorptive capacity of peanut shells increased with the decrease in the pH of the solution (pH 2.5 showed the highest removal of the Brown acid dye). The contact time with the highest efficiency in dye removal was 90 minutes. However, with 10 minutes of adsorption, 92.3% of the dye was already removed, and there was no significant increase in removal efficiency between 10 min and 90 min. Thus, it is recommended the use of 10 min of adsorption.

The smallest masses of peanut shell showed greater efficiency in removing the Brown acid dye, which was related in this study to the release of colored substances by the adsorbent material, due to the similar color of the peanut shells compared to the evaluated dye. The highest sorption capacity of dye by the peanut shell was 7.753 mg/g, corresponding to 93% removal. This result was obtained when the lowest peanut shell mass was added (0.3 g). The results demonstrate that the biosorbent is a viable alternative for the removal of Brown acid dye.

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References

1. É. Hansen, P.M. de Aquim, M. Gutterres; Environmental assessment of water, chemicals and effluents in leather post-tanning process: A review, *Environ Impact Asses.* **89** 2021. <https://doi.org/10.1016/j.eiar.2021.106597>.
2. J.S. Piccin, L.A. Feris, M. Cooper, M. Gutterres; Dye Adsorption by Leather Waste: Mechanism Diffusion, Nature Studies, and Thermodynamic Data, *Journal of Chemical & Engineering Data* **58** 873–882, 2013. <https://doi.org/10.1021/je301076n>.
3. M.V.B. Zaroni, H. Yamanaka; Corantes: Caracterização química, toxicológica, métodos de detecção e tratamento, 1st ed., Cultura Acadêmica, 2016.
4. B. Mella, M.J. Puchana-Rosero, D.E.S. Costa, M. Gutterres; Utilization of tannery solid waste as an alternative biosorbent for acid dyes in wastewater treatment, *Journal of Molecular Liquids* **242** 137–145, 2017. <https://doi.org/10.1016/j.molliq.2017.06.131>.
5. É. Hansen, P. Monteiro de Aquim, A.W. Hansen, J.K. Cardoso, A.L. Ziulkoski, M. Gutterres; Impact of post-tanning chemicals on the pollution load of tannery wastewater, *Journal of Environmental Management* **269** 110787, 2020. <https://doi.org/10.1016/j.jenvman.2020.110787>.
6. S. Ortiz-Monsalve, P. Valente, E. Poll, V. Jaramillo-García, J.A. Pegas Henriques, M. Gutterres; Biodecolourization and biodegradation of dye-containing wastewaters from leather dyeing by the native fungal strain *Trametes villosa* SCS-10, *Biochemical Engineering Journal* **141** 19–28, 2019. <https://doi.org/10.1016/j.bej.2018.10.002>.

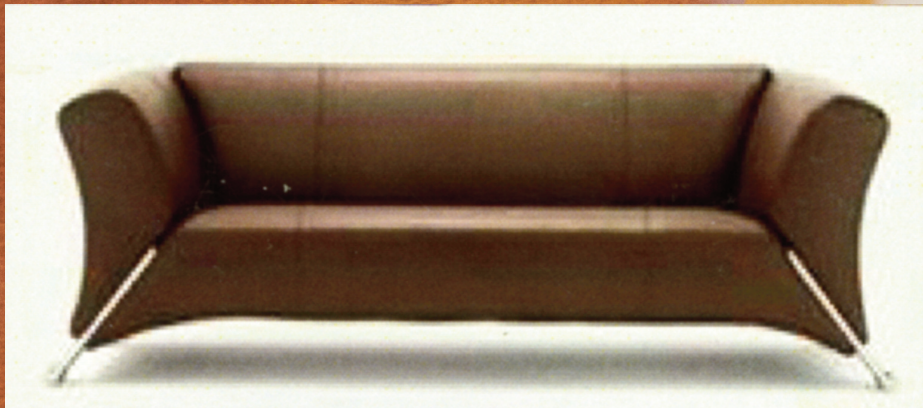
7. É. Hansen, P. Monteiro de Aquim, M. Gutterres; Current technologies for post-tanning wastewater treatment: A review, *Journal of Environmental Management* **294**, 113003, 2021. <https://doi.org/10.1016/j.jenvman.2021.113003>.
8. A. de la Luz-Pedro, E.F. Martínez Prior, M.H. López-Araiza, S. Jaime-Ferrer, A. Estrada-Monje, J.A. Bañuelos; Pollutant Removal from Wastewater at Different Stages of the Tanning Process by Electrocoagulation, *Journal of Chemistry* **2019**, 1–9, 2019. <https://doi.org/10.1155/2019/8162931>.
9. V. Kozik, K. Barbusinski, M. Thomas, A. Sroda, J. Jampilek, A. Sochanik, A. Smolinski, A. Bak; Taguchi Method and Response Surface Methodology in the Treatment of Highly Contaminated Tannery Wastewater Using Commercial Potassium Ferrate, *Materials* **12**, 3784, 2019. <https://doi.org/10.3390/ma12223784>.
10. M. Moreira, E. Hansen, G. Giacomolli, F. Morisso, P. Aquim; Evaluation of Chemical Products in Leather Post-tanning Process and Their Influence in Presence of Neutral Salts in Raw Tannery Effluent, *JALCA* **114**(4) 108–117, 2019.
11. M. Pal, M. Malhotra, M.K. Mandal, T.K. Paine, P. Pal; Recycling of wastewater from tannery industry through membrane-integrated hybrid treatment using a novel graphene oxide nanocomposite, *Journal of Water Process Engineering* **36**, 101324, 2020. <https://doi.org/10.1016/j.jwpe.2020.101324>.
12. A.C.C. Pena, C.B. Agustini, L.F. Trierweiler, M. Gutterres; Influence of period light on cultivation of microalgae consortium for the treatment of tannery wastewaters from leather finishing stage, *Journal of Cleaner Production* **263**, 121618, 2020. <https://doi.org/10.1016/j.jclepro.2020.121618>.
13. R. Suthanthararajan, E. Ravindranath, K. Chits, B. Umamaheswari, T. Ramesh, S. Rajamam; Membrane application for recovery and reuse of water from treated tannery wastewater, *Desalination*. **164**, 151–156, 2004. [https://doi.org/10.1016/S0011-9164\(04\)00174-2](https://doi.org/10.1016/S0011-9164(04)00174-2).
14. S. Tamersit, K.-E. Bouhidel, Z. Zidani; Investigation of electro dialysis anti-fouling configuration for desalting and treating tannery unhairing wastewater: Feasibility of by-products recovery and water recycling, *Journal of Environmental Management* **207**, 334–340, 2018. <https://doi.org/10.1016/j.jenvman.2017.11.058>.
15. C.V.T. Rigueto, M. Rosseto, D.D.C. Krein, B.E.P. Ostwald, L.A. Massuda, B.B. Zanella, A. Dettmer; Alternative uses for tannery wastes: a review of environmental, sustainability, and science, *J Leather Sci Eng.* **2**, 21, 2020. <https://doi.org/10.1186/s42825-020-00034-z>.
16. M. Kadhom, N. Albayati, H. Alalwan, M. Al-Furaiji; Removal of dyes by agricultural waste, *Sustainable Chemistry and Pharmacy* **16**, 100259, 2020. <https://doi.org/10.1016/j.scp.2020.100259>.
17. D.L. Pavia, G.M. Lampman, G.S. Kriz, J.R. Vyvyan; Introduction to Spectroscopy, 5th ed., Cengage Learning, 2014.
18. O. Bobet, S. Nassio, M. Seynou, B. Remy, L. Zerbo, I. Sanou, M. Sawadogo, Y. Millogo, E. Gilles; Characterization of Peanut Shells for Their Valorization in Earth Brick, *JMMCE*. **08**, 301–315, 2020. <https://doi.org/10.4236/jmmce.2020.84018>.
19. A.D.S. Nunes; Production of adsorbents from peanut shell for use in the removal of organic dyes, UESB, 2014.
20. J. Song, W. Zou, Y. Bian, F. Su, R. Han; Adsorption characteristics of methylene blue by peanut husk in batch and column modes, *Desalination*. **265**, 119–125, 2011. <https://doi.org/10.1016/j.desal.2010.07.041>.
21. A.R. Buist, A.R. Kennedy; Salt forms of the pharmaceutical amide dihydrocarbamazepine, *Acta Crystallographica. Section C, Crystal Structure Communications* **72**, 155–160, 2016. <https://doi.org/10.1107/S2053229616001133>.
22. E. Sterenzon, V.K. Vadivel, Y. Gerchman, T. Luxbacher, R. Narayanan, H. Mamane; Effective Removal of Acid Dye in Synthetic and Silk Dyeing Effluent: Isotherm and Kinetic Studies, *ACS Omega* **7**, 118–128, 2022. <https://doi.org/10.1021/acsomega.1c04111>.
23. D. Garg, S. Kumar, K. Sharma, C.B. Majumder; Application of waste peanut shells to form activated carbon and its utilization for the removal of Acid Yellow 36 from wastewater, *Groundwater for Sustainable Development* **8**, 512–519, 2019. <https://doi.org/10.1016/j.gsd.2019.01.010>.
24. J.M.H.F. Barros, L.F. Correia, A.F. Marinho, G.Z. Clericuzi, K.S.M.G. de Sousa; Use of Peanut Shell as Adsorbent in Removing the Methylene Blue, *BJD*. **6**, 79370–79384, 2020. <https://doi.org/10.34117/bjdv6n10-389>.
25. J. Rashid, F. Tehreem, A. Rehman, R. Kumar; Synthesis using natural functionalization of activated carbon from pumpkin peels for decolourization of aqueous methylene blue, *Science of The Total Environment* **671**, 369–376, 2019. <https://doi.org/10.1016/j.scitotenv.2019.03.363>.
26. J. Georgin, G.L. Dotto, M.A. Mazutti, E.L. Foletto; Preparation of activated carbon from peanut shell by conventional pyrolysis and microwave irradiation-pyrolysis to remove organic dyes from aqueous solutions, *Journal of Environmental Chemical Engineering* **4**, 266–275, 2016. <https://doi.org/10.1016/j.jece.2015.11.018>.
27. G.D. Orsoletta; Aproveitamento Tecnológico da Casca de Amendoim em Processo de Biossorção de Corante Têxtil, Universidade Tecnológica Federal do Paraná, 2017.
28. R. Gong, Y. Ding, M. Li, C. Yang, H. Liu, Y. Sun; Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution, *Dyes and Pigments* **64**, 187–192, 2005. <https://doi.org/10.1016/j.dyepig.2004.05.005>.
29. A. Soltani, M. Faramarzi, S.A. Mousavi Parsa; A review on adsorbent parameters for removal of dye products from industrial wastewater, *Water Quality Research Journal* **56**, 181–193, 2021. <https://doi.org/10.2166/wqrj.2021.023>.
30. A.V. Baskar, N. Bolan, S.A. Hoang, P. Sooriyakumar, M. Kumar, L. Singh, T. Jasemizad, L.P. Padhye, G. Singh, A. Vinu, B. Sarkar, M.B. Kirkham, J. Rinklebe, S. Wang, H. Wang, R. Balasubramanian, K.H.M. Siddique; Recovery, regeneration and sustainable management of spent adsorbents from wastewater treatment streams: A review, *Science of The Total Environment* **822**, 153555, 2022. <https://doi.org/10.1016/j.scitotenv.2022.153555>.
31. V.S. Silveira, A.S. de Vargass, É. Hansen, L.C. Robinson, N.A. Thoen, D.M. de Quevedo, E.L. Schneider, P.M. de Aquim; Novel solidification/stabilization process of wet blue leather waste to produce recycled lightweight aggregates, *Waste Biomass Valor.* 2022. <https://doi.org/10.1007/s12649-022-01869-9>.

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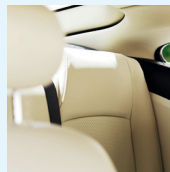


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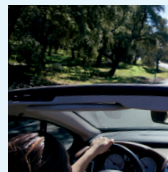
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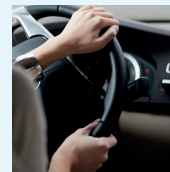
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Lifelines

Nan Sun received his high school degree from Daqing Foreign Language School in 2019. Now he is pursuing his B.S. degree in Light Chemical Engineering at Sichuan University. His current research focuses on the cleaner leather production.

Ji-bo Zhou, see *JALCA* 113, 198, 2018.

Xue-pin Liao, see *JALCA* 113, 198, 2018.

Bi Shi, see *JALCA* 99, 220, 2004.

Samantha Feron de Moraes, Chemical engineering undergraduate student at Unisinos university. She works with solid waste management in the chemical industry, seeking to reduce the generation of industrial waste.

Patrice Monteiro de Aquim, professor and researcher at Feevale University. She holds a degree in Chemical Engineering (2002, Pontifical Catholic University of Rio Grande do Sul), Master's in Chemical Engineering (2004), and PhD in Chemical Engineering (2009, Federal University of Rio Grande do Sul). She works mainly on the following topics: leather, tanneries, minimization of effluents, environment, energy and water reuse.

Bethania Brochier, professor of the Chemical Engineering and Food Engineering undergraduate courses at the University of Vale do Rio dos Sinos (Unisinos). She holds a degree in Food Engineering

(Unisinos), Master's and PhD in Chemical Engineering (Transport Phenomena and Unit Operations, from Federal University of Rio Grande do Sul). She has experience in the areas of Food Science and Technology and Food Engineering.

Amanda Gonçalves Kieling, professor at Unisinos University, coordinator of the Environmental Engineering course and the Environmental Management course. She holds a degree in Food Engineering (2006, Unisinos University), Master's in Civil Engineering (2009, Unisinos University), and PhD in Engineering (2016, Federal University of Rio Grande do Sul). She has experience in the area of Food Science and Technology, working mainly with Quality Management and Waste Management, in particular: rice husk ash, foundry waste, sugarcane waste and organic waste, working to transform waste into co-products.

Éverton Hansen, professor of Chemical Engineering at the Universidade do Vale do Rio dos Sinos (Unisinos) and the Centro Universitário Ritter dos Reis (UniRitter). He holds a degree in Chemical Engineering (2013, Federal University of Rio Grande do Sul), Master's in Materials Technology and Industrial Processes (2016, Feevale University), and PhD in Chemical Engineering (2021, Federal University of Rio Grande do Sul). He has experience in the leather industry, working mainly on the following topics: water reuse, characterization and treatment of liquid effluents and management of contaminated areas.

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